IMPACT OF A LONG-TERM CAUSTIC DISCHARGE FROM RED MUD DISPOSAL ON A FRESHWATER LAKE

by

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DECLARATION

I certify that the work described in this thesis is my own, except where otherwise stated, and has not been previously submitted for a degree at this, or any other, University.

Ronald A. Edwards

A B S T R A C T

Kinghorn Loch is a small lake of area 11.3 ha and maximum depth 12.8 m, situated in Fife Region of Scotland. From 1947-1983 the loch was polluted by leachate from Red Mud disposal. Red Mud is a waste product of the alumina dressing industry. The leachate consisted of a highly alkaline solution of sodium hydroxide and carbonate and contained high levels of dissolved aluminium, arsenic, vanadium and sulphate.

Initially the loch became nutrient enriched (mainly orthophosphate) but by 1961 the pH bagan to increase significantly so that by 1983 it exceeded a mean of pH 10.1, and levels of dissolved arsenic and vanadium were the highest of any watercourse in the U.K. During this time 0.5 m of red/red-brown fine mud accumulated, at a rate which by 1983 was in excess of 25 mm yr^{-1} (1.5 kg m^{-2} yr^{-1}). Aluminium in the leachate reacted with high levels of native silicon and magnesium to produce authigenic clay minerals. At near-neutral pH these proved to be high in silicon but by 1983 magnesium was dominant. The progression from high-Si to high-Mg seems to have been continuous and does not suggest the formation of discrete mineral phases. By 1983 authigenic clay minerals represented 24% of sediment mass, while organic material, generated by prolonged and severe phytoplankton blooms, accounted for 16% and detrital inputs 12%. Calcite, precipitated from the native water, made up 48% of the sediment. Experimental procedures found that calcite production was essentially abiotic and proceeded by second order kinetics. Precipitation of clay minerals was independant of calcite production and calcite did

not incorporate significant quantities of organic matter.

The high organic input, combined with hematite (washed-in as Red Mud solids), caused highly reducing conditions within the sediment, but the red colour indicated Fe(III) dominance, while interstitial sulphate was not fully reduced. In some cores a grey zone occured immediately above the native sediment and this indicated extensive pyrite formation. However, despite the high level of sulphate in the loch water, the lack of extensive sulphate reduction led to low sulphur levels in the polluted profile. The interstitial water was found to be chemically active, with high levels of dissolved iron, calcium, magnesium, aluminium and arsenic occuring.

The leachate was diverted from the loch in 1983 and the water quality recovered quickly. By 1984 the pH had returned to a natural pH 8. However by 1985 arsenic levels in the water remained substantially elevated (30-50 ug l^{-1}) and although sediment core profiles were found to be much less reducing, interstitial water chemistry was active, and dissolved arsenic levels exceeded 1 mg l^{-1}, which was passed to the body of the loch.

A thermodynamic model was developed to determine the chemical speciation of mixed waters and to calculate the degree and character of mineral deposition. However, due to the lack of available kinetic data, application of the model was limited.

Benthic populations were extremely restricted in 1983 but although greatly increased in numbers by 1985, no diversification had occured. Plankton and benthic invertebrates (in 1985) did not concentrate

arsenic.

The high authigenic content of the sediments provides a unique opportunity for the further study of clay mineral formation over a very short time span, and allows a consideration of pH dependance of such processes.

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DEFINITION OF NON STANDARD UNITS

Physical quantity	Name of unit	Symbol for unit	Definition of unit
temperature, t	degree Celsius	^{o}C	$t\{^{o}C\}=t\{K\}-273.16$
area	hectare	ha	$10^{4}m^{2}$
volume	litre	l	$10^{-3}m^{3}$

ABBREVIATIONS USED IN THE TEXT

abbreviation	meaning
F.R.P.B.	Forth River Purification Board
c.l.	confidence limit (at 95% unless stated otherwise)
s_w	within batch standard deviation
s_b	between batch standard deviation
s_t	total standard deviation
L.O.D.	limit of detection (4.65x s_w unless stated otherwise)
A.V.S.	acid volatile sulphur
B.O.D.	5 day biochemical oxygen demand
C.O.D.	chemical oxygen demand

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For a study of this nature, particularly when attempted on a part-time basis, it is inevitable that thanks will be due to a large number of people who have given assistance.

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Finally, and most of all, to my wife, Marilyn, and children, Rhian, Siân and Owain, who have suffered this study, probably more so than me, and have come out on top.

CHAPTER ONE

INTRODUCTION

1.1. GENERAL DESCRIPTION OF THE STUDY AREA

Kinghorn Loch is a small lake situated 1.5 km W.N.W. of the Burgh of Kinghorn within the Fife Region of Scotland and 13.3 km due north of the City of Edinburgh. It has a surface area of 11.3 ha and a maximum depth of 12.8 m. Since 1947 the loch has been the recipient of a highly alkaline discharge issuing from nearby Whinnyhall Tip, a landfill site operated by BA Chemicals Ltd., part of British Alcan Aluminium Company Limited, for the disposal of red mud.

Red mud is a waste product of bauxite dressing by the Bayer process during the production of alumina. It consists of iron and clay solids, being that part of the bauxite insoluble in concentrated sodium hydroxide at high temperature and pressure. However it also contains an aqueous phase (approximately 45% wet weight) comprising alkali not removed by the mud washing process. This phase contains alkali at a concentration of approximately 0.4 M and pH 13.4. The aqueous phase, in contrast to the solids, contains a proportion of all those ions which were dissolved from the bauxite including aluminium, arsenic, vanadium, sulphur, selenium, phosphorus, fluorine, and silicon. In addition commercial quality sodium hydroxide can contain mercury as a contaminant but none has been found during the study.

1.1.1. HISTORY OF POLLUTION.

Tipping of the material at Whinnyhall began in 1944-45 when the original coastal tip, operated since 1917, became filled. Drainage from this elevated site had been arranged by re-routing at least one spring to Kinghorn Loch. However by 1951 percolate was beginning to appear through the south wall of the tip and this seeped down the hillside to the Kirkton Burn and thence flowed west to the Firth of

Forth. This discharge quickly destroyed vegetation, including trees and was finally channelled to the burn in a system of drains.

By 1983 these two discharges, illustrated in Figure 1.1, had destroyed aquatic life in the Kirkton Burn and severely limited life in Kinghorn Loch. The leachate to the Kirkton Burn appeared to be "pure" leachate containing a little rain water percolate, and is the more alkaline of the two, averaging pH 12.8. Leachate to Kinghorn Loch averaged pH 12.1 due to its prior mixing with native spring water and was considerably lower in dissolved organic matter. By 1983 the pH of the loch had reached a level in excess of pH 10.

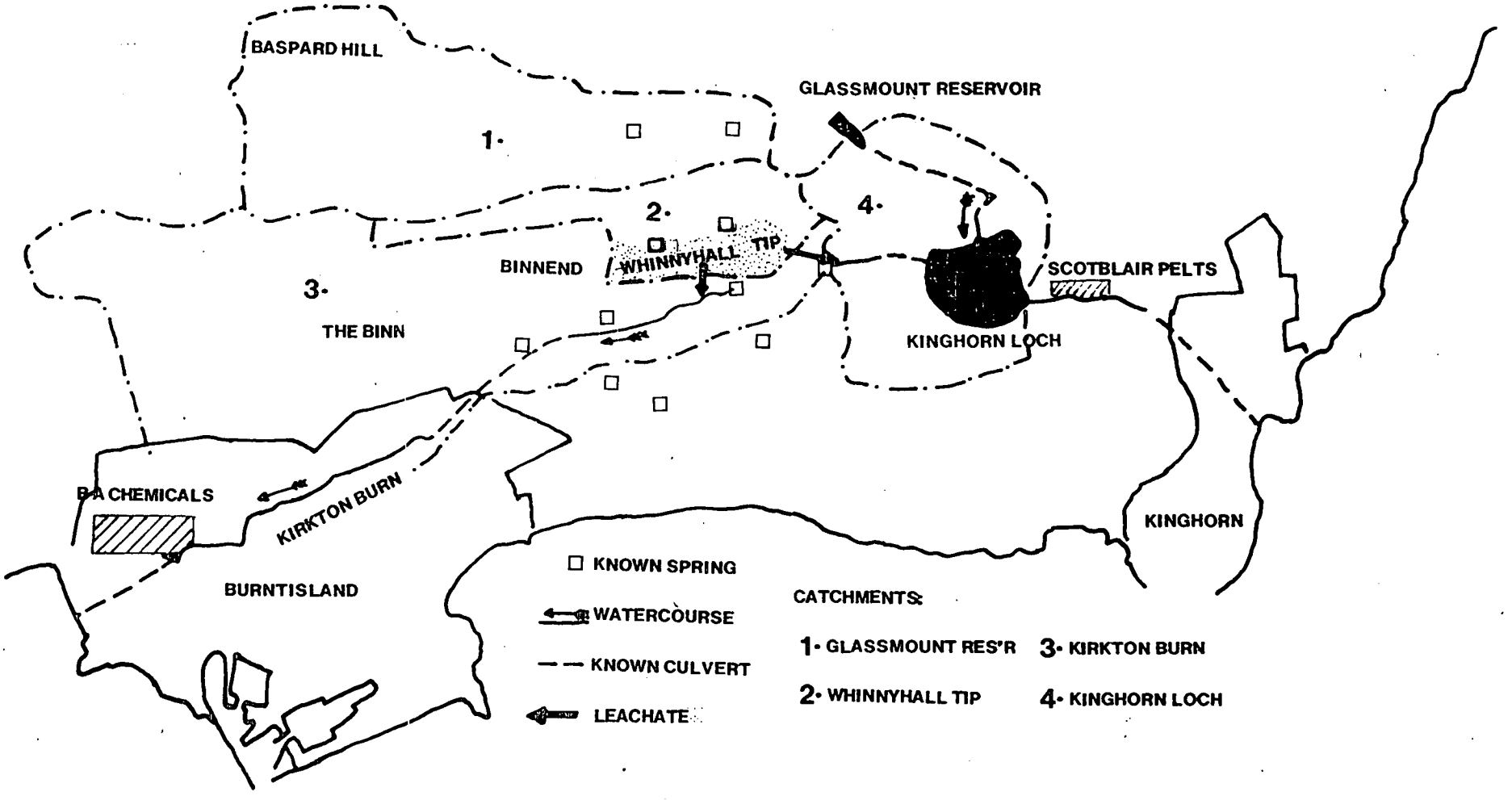
1.1.2. RECOVERY FROM POLLUTED STATE.

On the 25th May 1983, three years into the present study, this discharge was removed from the loch as part of a scheme designed to present the leachate for suitable treatment and disposal elsewhere. At the time of writing it is being pumped to the Kirkton Burn catchment to join its sister leachate. Proper disposal of the discharges is envisaged within an agreed timetable.

1.2. PREVIOUS WORK

Previous study of the loch had consisted almost entirely of the routine, and essentially passive, chemical analysis of the state of the water and of the incoming leachates performed by the F.R.P.B. Such analyses were carried out four times a year at best, and prior to 1978 were even less frequent. In 1978 the F.R.P.B. determined to improve the state of Kinghorn Loch and Kirkton Burn by the removal and proper treatment of the leachates. Chemical analytical effort was concentrated on the higher pH leachate to the Kirkton Burn and

FIGURE 1.1. Map showing the study area indicating locations named in the text



work, carried out in conjunction with BA Chemicals Ltd. was co-ordinated by the present author as an employee of the Board. It was intended to devise a treatment process more suited to the situation of the burn, than had been proposed by consultants to the company. This led to a conserted analytical effort with regard to the Kirkton Burn and confirmed that conceptually suitable treatment processes were available and considered economically viable.

The Biology Section of the F.R.P.B. had carried out faunal and floral surveys of the loch at intervals of 2-3 years. Weed sweep, benthic grab and plankton netting had been employed. The results had been used to detail the decline in biological activity and diversity in the loch.

1.3. AIMS OF THE STUDY

The primary aims have been to collate historical information and to provide analytical data, particularly chemical and geochemical but also ecological, in order to describe the situation found in the loch and its sediments prior to rehabilitation, and to follow, as far as the short duration of the study would allow, its recovery. To this end the development of a chemical speciation model was undertaken in order to endeavour to conclude what mineralization might occur and to quantify the chemical deposition of sediments.

The situation of the loch as an enclosed freshwater body of long residence time, and the way in which it received the discharge appears to be unique. Red mud is often disposed of by discharge to marine lagoons and the effect on the marine environment has been studied by several workers including Baseden[1] in Australia and

Hamada[2] in Japan. Burrows[3], in reviewing the marine ecological effects of red mud found that the presence of such a large quantity of extremely fine red mud caused ingestion problems for organisms that swamped any other effects. Effects due to ionic aluminium were also limited by the buffering capacity of the sea water.

In Kinghorn Loch only limited quantities of red mud reached the loch and the sediment load was derived from reaction with spring waters prior to reaching the loch and within the loch water itself. The buffering within the loch was in favour of the soluble ions present in the leachate as the natural waters have little buffering capacity. Thus the system has provided an opportunity to study chemical processes such as carbonate mineral formation and aluminosilicate formation and diagenesis under chemically favourable environmental conditions.

CHAPTER TWO

ORIGIN AND CHEMICAL COMPOSITION OF RED MUD AND ASSOCIATED LIQUOR

2.1. ORIGIN

The Burntisland plant of BA Chemicals Limited has been in existence since 1917 in which year it produced 10,000 tonnes of alumina. By 1980 production had risen to 120,000 tonnes of high quality grades of alumina. Between 1950 and 1970 an increasing proportion of the output was for special (chemical) grades of milled and unmilled alumina and alumina trihydrate. Much of the information contained in this section has been provided by BA Chemicals Limited in its publication "Alumina Chemicals from Burntisland"[4] or by private communication.

Bauxite used at the plant is imported primarily from Awaso in Ghana. Approximately 52% by weight of the alumina is in the form of the trihydrate, $Al_2O_3.3H_2O$, while the remainder is as the monohydrate. The trihydrate may be extracted at temperatures of 100°C to 145°C while the monohydrate requires temperatures of 180°C to 250°C. The bauxite is processed as shown in Figure 2.1 whereby crushed bauxite is milled in the presence of concentrated sodium hydroxide solution and then heated under pressure in a series of vertical autoclaves, or "kiers". The pressure is reduced in a series of flash vessels. Spent liquor from mud washing is added and the liquor desanded and desilicated, a process which allows removal of fine silica onto the mud. Starch is added as a flocculent and the mud thickened in stirred tanks before the liquor is clarified on Kelly pressure filters using lime as a filter aid. The liquor then proceeds to become supersaturated at lower temperatures whereby seeding recovers the pure hydrate.

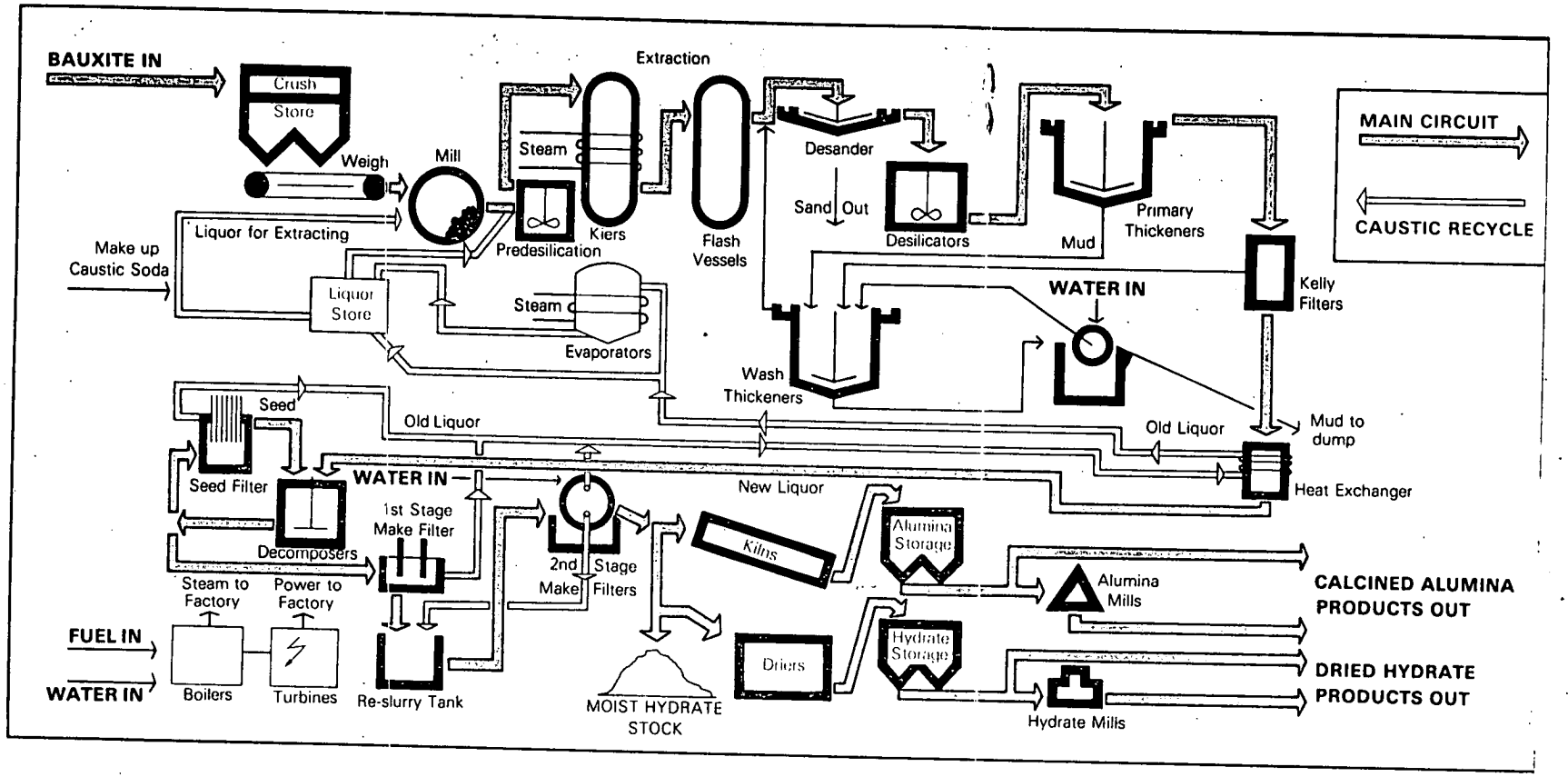


FIGURE 2.1. The Bayer Process (Burntisland Flow Sheet). Reproduced by permission of BA Chemicals Ltd.

The mud from the Kelly filters and primary thickeners is passed counter-current through a washing process whereby mud is slurried with water and pumped to a series of wash thickeners where the wash overflows and the mud is continuously removed from the tank bottom. The wash and mud travel in opposite directions thus progressively reducing the alkali content of the mud liquor. The mud is filtered and washed on a rotary drum vacuum filter and the mud cake scraped from the drum for disposal. This process is capable of producing a mud of 35-45% moisture content wet weight[4,5]. Huge quantities of red mud are produced; in 1980, 280,000 tonnes of bauxite was consumed by the plant for 120,000 tonnes of alumina produced. This is not an unreasonable ratio considering the high grade of alumina manufactured and compares with other (mostly smelter) plants which, depending on the source of bauxite, generate between 0.3 and 2.5 tonnes of red mud per tonne of bauxite and averages about 1 tonne per tonne[5].

This mud, which is relatively dry compared to that from conventional processes should be capable of dry stacking, a system whereby the height of waste is gradually raised by constructing an empounding dyke (of consolidated red mud or other source material) on top of each consolidated layer. By this means stacking heights of 30 m are possible[5]. In order to avoid contamination of ground and surface waters the site should be sealed. Unfortunately no such control was applied with the development of Whinnyhall Tip in the early stages and the problems were compounded by the covering of natural springs and the failure to provide a rain shedding surface to areas not in use.

To date only the east end of the site has been used and the relative flows of the leachates have varied depending on the location of the dumping within the site. It is probable that the site will be developed westwards but, since this is heading onto more elevated ground, adequate planning and control of tipping will be essential.

Red mud has considerable potential as a raw material particularly for the recovery of iron and titanium in commercially viable quantities. Attempts to utilise it on this scale have however been thwarted by the problems of smelting such a high soda material. Patents have been issued with the intention of overcoming these problems, one of interest may be that of Lakatos et al[6], whereby ferric sulphate is used to ion exchange sodium from the original level of 9.6% (as Na_2O) in the (dry) mud to 0.7%, while increasing iron from 39.2% (as Fe_2O_3) to 46.9% of the mud; thus making it suitable for smelting. Further references (e.g. Logomerac[7]) suggest that red mud may form a useful raw material for the recovery of rare earth elements niobium (300-9100 mg kg^{-1}), lanthanum (200-12000 mg kg^{-1}), yttrium (15-4500 mg kg^{-1}) and scandium (24-1700 mg kg^{-1}). The figures inside brackets indicate the range of values found in red mud from different sources (dry weight). Thus, one day, red mud from Whinnyhall Tip may be reworked as a raw material in its own right.

Up until May 1983 red mud slurry as deposited at Whinnyhall Tip presented Kinghorn Loch with an incoming stream (of mean flow 2.7 l s^{-1}) containing four distinctly different polluting loads. These were, in order of importance:

caustic liquor

chemically deposited solids

red mud solids

burnt blaes

The origin of these different loads will be considered below and be followed by a consideration of their distinctive chemical characteristics.

The stream drained from the tip area via an unknown system of underground channels or culverts and passed through the retaining wall by means of a pipe. The stream proceeded into a cutting (of the disused mineral railway to the oil shale workings) where it was ponded into a narrow settlement pond of some 60 m^3 capacity. The pond was retained by a concrete dam containing a sluice plate fitted with a 'V' notch flow-measuring weir.

The pond offered a retention time of approximately 6 hours under normal conditions, but considerably less in spate. The pond became filled with solids very quickly thereby short-circuiting any significant retention and, although periodically cleaned out by the company, generally issued suspended solids at 7-420 mg l^{-1}, with a mean of 87 mg l^{-1}, to the loch. The suspended solids load of this leachate would contribute 7000 kg (dry weight) of solids each year, 80-85% of which will be seen later to be calcium carbonate. Data contained in Table 4.6 indicate that an estimated $7x10^4$ kg carbonate mineral and $4x10^4$ kg aluminosilicate (taking the structure proposed in Chapter 5.7.3) are chemically precipitated in the loch each year. Additionally however, quite often, at least four times a year,

vandals managed either to dislodge or remove the sluice plate allowing the slurry-like contents of the pond to flood into the loch. This load may be seen to contain virtually all of the iron entering the loch. It consisted of fine red mud solids intermixed with authigenically produced material and, given a mean iron content in the sediments (Table D.1) of approximately 2.5% as Fe, represents an input of 8500 kg yr^{-1} of clay minerals and 6200 kg yr^{-1} as Fe_2O_3 (from Table 2.7).

The overall sedimentation rate within the loch, originating from all sources including internal chemical and biological precipitation will be seen to be extremely variable. It will depend largely on the state and proper functioning of the settlement pond and on the quantity and strength of the incoming leachate. Apart from the generalization that the leachate will be strongest when tipping is occuring in the north-east sector of the tip and will be most voluminous in winter little is known of the precise factors affecting its character. Chemical and hydrological data were sparse prior to this study and would certainly not allow any quantitative assessment. It will be seen from Chapter 2.2.1 and Appendix A that despite weekly sampling since January 1981 the ability to measure the loadings involved is possible only within wide confidence limits and the task of understanding and quantifying the processes occuring within the system is thereby made more difficult.

2.2. CHEMICAL COMPOSITION

2.2.1. CAUSTIC LIQUOR

The aqueous phase of the leachate results from the mixing and subsequent reaction of red mud liquor with the natural spring waters,

diluted, to some extent, by rain water. The origin and composition of the natural water will be discussed in Chapter 3. Table 2.1 sets out a typical analysis of interstitial water from freshly generated red mud sampled before tipping.

pH	13.5	
sodium	8990	
aluminium	3560	
potassium	14.5	
magnesium	2.0	
calcium	<1	
chloride	130	
arsenic	26	
vanadium	13	
silicon	7.9	as Si
orthophosphate	5.6	as P
nitrate+nitrite	5.0	as N
fluoride	1.7	
ammonia	1.0	as N
organic carbon	<0.5	%

TABLE 2.1 Typical analysis of interstitial water taken from new red mud.
(results in mg/l unless stated otherwise)

Interstitial water was extracted by pressure filtration through a glass fibre disc (Whatman grade C) that had been previously washed with 1 M sodium hydroxide, thoroughly rinsed with water and dried under vacuum. The filtrate was then passed through a 0.45 um polycarbonate membrane. This procedure produced a clear, colourless liquid. This was in contrast to the leachates which were deep brown in colour. Organic carbon was measured by reducing the pH of an aliquot to near pH7 with 1 M hydrochloric acid and thence to pH 4.0 with 0.1 M hydrochloric acid whilst bubbling nitrogen through the solution. The gas purge was continued for one hour to remove all residual carbon dioxide. The pH was adjusted to 7 (with 0.1 M carbonate-free sodium hydroxide) and the solution reduced to dryness in an oven at 95°C. The dry material was ground in a mortar and

pestle and analysed for carbon (as described in Chapter 9.3).

The fact that the interstitial water was clear and very low in organic matter was surprising since it would be expected to contain dissolved humic material from the bauxite and also possibly starch. However it is asserted[4] that the Bayer process causes breakdown of bauxite humic materials into lower organic acid salts and carbon dioxide. Any residual salts so formed are removed into the red mud as the calcium salt during liming. Unfortunately it was not until November 1984 that the facility for carbon analysis became available and this matter had not been pursued. Subsequently one sample was taken for each of four months specifically for carbon analysis and it was found that the level of organic carbon was insignificant in each case.

Back records of the F.R.P.B. showed that the leachate to the Kirkton Burn had always possessed a very high biochemical oxygen demand (BOD_5) and 4-hour permanganate value (see Chapter 9.1.2.1 for analytical methodology) of between 52 and 157 mg l^{-1}oxygen, with a mean of about 90 mg $l^{-1}O$. These parameters provide a measure of potential oxygen consumption by mild oxidative processes particularly that of labile organic material and reduced nitrogen compounds. The discharges were atypical of the waters normally subjected to these tests so the results must be treated with caution. However the discharges did not appear to contain any components that are known to interfere or bias the results. The leachate proceeding to Kinghorn Loch had always carried a lesser amount of degradable organic material, with values ranging from 1 to 29 mg l^{-1}oxygen and a mean of about 8 mg $l^{-1}O$. Interestingly the caustic effluent from the factory at Burntisland

gave a range of <0.3 to 17 mg $l^{-1}O$ with a mean of about 4 mg $l^{-1}O$. It is likely that this effluent contained material originating from sources other than waste liquor, a portion of which may be organic. It is evident that the leachates, particularly that to the Kirkton Burn, became enriched in organic matter during their percolation through the red mud and ultimately to the discharge point. It is likely that nearly all this material was dissolved from soil organic matter by the highly caustic liquor. The colour was not associated with iron compounds since iron, though extremely abundant in the red mud, was absent in the liquor and leachates. Table 2.2 illustrates a typical analysis of the leachate going to the Kirkton Burn.

pH	13.1	
sodium	10690	
aluminium	177	(dissolved)
potassium	8.9	
magnesium	1.9	(total)
calcium	2.0	(total)
arsenic	18	(total)
vanadium	31	(total)

TABLE 2.2 Typical analysis of leachate to Kirkton Burn. (results in mg/l)

Figure 2.2. charts the variation in pH of the leachates since 1977, and indicates the incorporation of the Kinghorn Loch flow into that to the Kirkton Burn in May 1983. Data available prior to 1981 were inadequate to allow any trend analysis of leachate strengths.

The ratio of Al:Na was always very much lower in the leachates compared to that for the red mud interstitial water. Aluminium levels in the leachates were very variable ranging from as low as 11 mg l^{-1} up to 250 mg l^{-1} with a mean around 160 mg l^{-1}. For a similar concentration of sodium ions, red mud interstitial water contained a

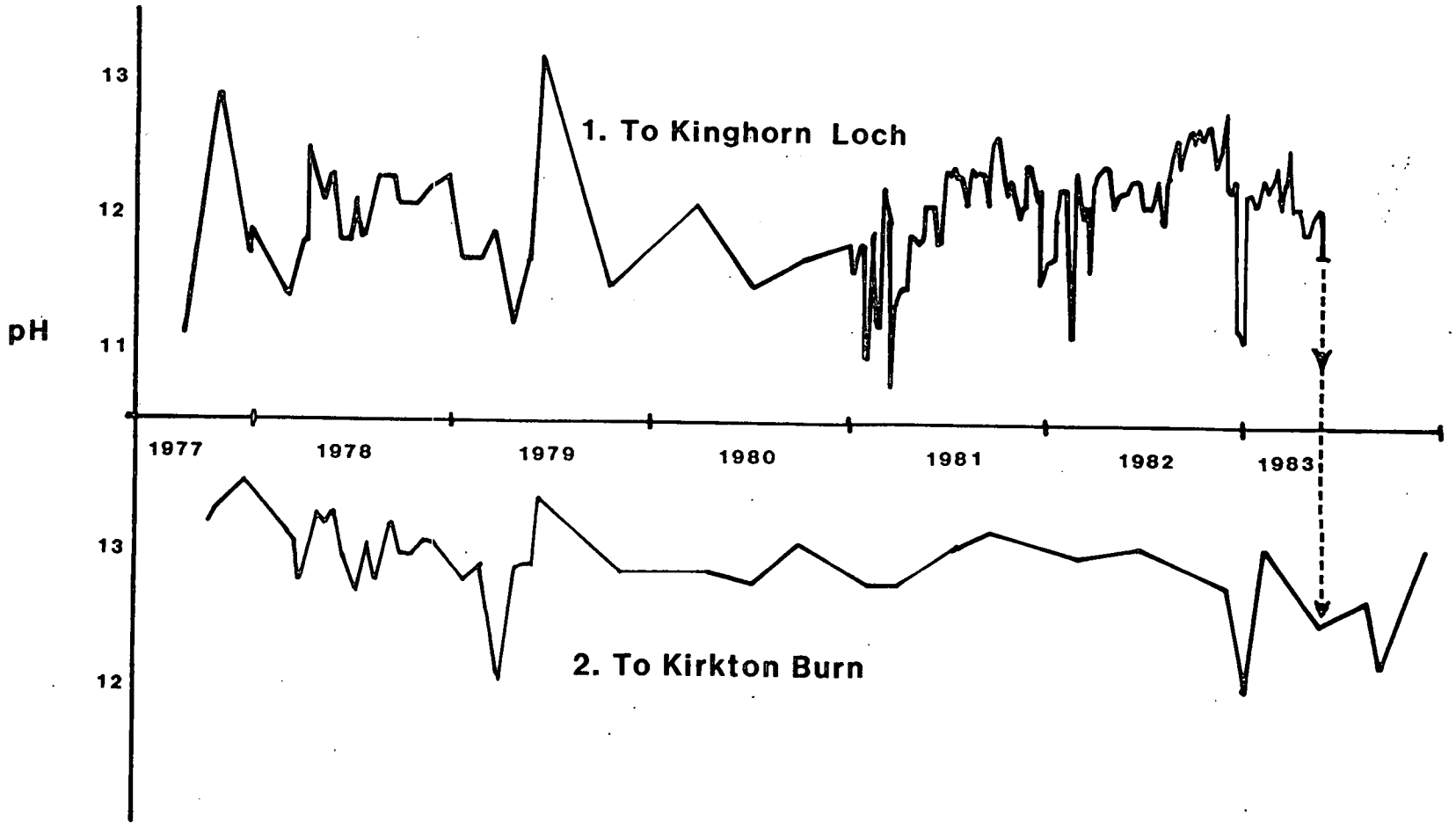


FIGURE 2.2. pH of leachates from Whinnyhall Tip (1977–1983)

relatively stable aluminium content of around 3560 mg l^{-1}. Since the leachates obtained virtually all their sodium and aluminium from the interstitial water it is evident that on passage from the tip to point of issue a mechanism existed for the removal of the bulk of the aluminium but not sodium.

It is unlikely that aluminium would be lost by flocculation processes involving organic matter, as humic material, taken into solution at high pH, would form anions carrying a considerable negative charge. This charge would be unmatched by the extremely small concentration of aluminium cations available.

The level of silicon in the red mud interstitial water was inadequate to cause any significant loss of aluminium by the formation of clays. However by consideration of thermodynamic data on the solubility of silica given by Stumm & Morgan[8] for the typical high pH reaction $4SiO_2(s)+4H_2O \leftrightarrows Si_4O_6(OH)_6^{2-}+2H^+$ it may be calculated that log K=-23.37 (for amorphous silica) and log K=-27.37 (for quartz). The data was based on 25°C in 0.5 M $NaClO_4$. Thus at pH 13 dissolution of amorphous silica could generate well in excess of 1 M dissolved silicon, while for quartz this would be 0.04 M, and 0.4 M at pH 13.5. It is therefore evident that, even giving due consideration to the inherent limitations of using thermodynamic data in this way, a solution of 0.04-1 M could be produced by dissolution of sand or silt in the substrate of the tip. Having shown that such an aluminium-silicon solution can be obtained, both must then be deposited to account for the low levels found in the leachates. Garrels & Christ[9](page 363) in a combination diagram of stability relations in the system Na_2O-Al_2O_3-SiO_2-H_2O (extrapolated from high

temperatures and pressures), indicated that albite was the most favoured aluminosilicate to be formed under such circumstances. However, at low temperature in aqueous solution, it is more likely that a hydrous mineral will form. Using data taken from Truesdell & Jones[10], the zeolite analcime is found to be thermodynamically more stable. No data was available for sodalites which would possibly give further stability. Thus at 25°C for the reaction

$$NaAlSi_2O_6.H_2O \text{ (analcime)} + 5H_2O \leftrightarrows Na^+ + Al(OH)_4^- + 2H_4SiO_4^o$$

log K=-12.701. For a sodium content of 0.4 M and aluminium of 0.13 M, 4×10^{-6} M silicon would be sufficient to produce analcime (given that activity coefficients of 0.8, 0.3, and 1 are aplicable to Na^+, $Al(OH)_4^-$ and $H_4SiO_4^o$ respectively as indicated by the speciation model of Chapter 6). Even a very low level of aluminium and silicon in the final leachate (say 10^{-4} M) would result in a propensity to deposit analcime or similar material. The rate determining step is likely to be dissolution of silica, but given even a modest degree of dissolution, it is evident that zeolite or clay minerals are likely to be formed whilst the leachates are flowing to the points of issue.

It is common for the relative abundances of arsenic and vanadium found in the red mud interstitial water to become reversed prior to issuing as the leachate to the Kirkton Burn. There is an apparent loss of arsenic within the aqueous system. This however, due to the relatively small number of data available, may not be significant. The loss of arsenic has been seen on several occasions and will be discussed later, but it is probable that arsenic is removed from solution onto the abundant iron mineral surfaces associated with red mud solids. That this removal of arsenic occurs within the system under study will become evident but that it should occur to such an

extent at such high pH values is surprising.

As the leachate percolates eastward towards Kinghorn Loch it encounters various underground springs of local hard water. The net effect of this is to reduce the pH and carbonate content of the leachate and to reduce the calcium and magnesium level in the spring water. Aluminium and silicon levels are also affected as is probably arsenic. The leachate leaving the settlement pond has been analysed on a weekly basis since January 1981 until its removal in 1983 and the results so obtained are collated in Table A.1 of Appendix A. An explanation of the statistical appraisal contained in the tables of Appendix A is included. The sampling programme was designed so as to give an estimate of the long-term mean that would be within 10% of its true value at 95% confidence limit. As far as the more important parameters are concerned this has marginally been achieved for aqueous concentrations though not for loadings. The Hydrology Section of the F.R.P.B. have additional monthly gaugings for the flow of leachate to Kinghorn Loch, for that of the north inlet (at Craigencalt Farm), and for that leaving the loch outlet but since chemical analysis and instantaneous flow are likely to be related, such additional flow data cannot be used in this context. The data have however been used to verify the accuracy of the weekly gauge-board readings. Mean loadings are within 20% of the predicted real situation. The sample taken on the 7th March 1983 has been omitted from the statistical appraisal as a pipe blockage was preventing leachate from leaving Whinnyhall Tip. The information contained in the tables of Appendix A will be further considered in sections on the chemical budget in the loch (Chapter 4) and for the mathematical modelling of the system (Chapter 6).

On several occasions samples were additionally analysed for heavy metals, parameters not contained in the routine monitoring programme. Tables 2.3. and 2.4. illustrate typical data obtained from this extended analysis for total and dissolved parameters respectively. The analytical techniques used for generating the chemical data are considered in Chapter 9.

Batches of the leachate to Kinghorn Loch were also treated as under Chapter 2.2.1. to determine the level of dissolved organic carbon and Table 2.5. illustrates the findings.

determinand	result	determinand	result
pH	11.8	suspended solids	67
iron	.22	manganese	.056
zinc	.009	nickel	.061
copper	.033	chromium	.105
lead	.033	cadmium	.012
vanadium	5.7	arsenic	3.6
aluminium	91.9		

TABLE 2.3. Concentration of total trace elements in the leachate to Kinghorn Loch (mg/l).

determinand	result	determinand	result
iron	.008	manganese	.0019
zinc	.0084	nickel	.08
copper	.06	chromium	.007
lead	.0011	cadmium	.00006
vanadium	5.7	arsenic	3.2
aluminium	92.5		

TABLE 2.4. Concentration of dissolved trace elements in the leachate to Kinghorn Loch (mg/l).

date taken	organic carbon	date taken	organic carbon
1-12-1982	7.5	20- 2-1983	5.2
9- 1-1983	<2	14- 4-1983	5.0

TABLE 2.5. Concentration of dissolved organic carbon in the leachate to Kinghorn Loch (mg/l).

It will be seen that the input of trace metals to the loch via the

leachate is very low indeed with the exception of aluminium, arsenic, and vanadium which are present at high concentrations as dissolved species. The lead contained in the leachate may, because of the uncertain effects of chemical separation techniques during bauxite processing and the protection of red mud from atmospheric input prior to dumping, be expected to contain an atypical isotopic ratio and therefore to be a source of error during radiochemical dating. The leachate would provide the loch sediment with approximately 18 mg kg^{-1} whilst Table D.1, in indicating a lead content in the sediment of 50 mg Pb kg^{-1}, requires a substantial additional supply of approximately 6 kg yr^{-1} Pb. Rowlatt[11] provides information on the supply of lead to lakes in the English Lake District. The lakes involved covered a wide range of human habitational influence and indicated a supply, to an area equivalent to Kinghorn Loch, of between 5 to 30 kg Pb each year. The source of the lead is stated as being mainly by atmospheric aerosol. Thus it is reasonable to assume that the bulk of the lead found in Kinghorn Loch sediments has an essentially similar origin, so that the possible chemical partitioning of lead and radionuclides in detrital red mud will not cause any gross bias in ^{210}Pb dating analysis.

The organic material dissolved in the leachate represents an input to the loch of approximately 58 kg each year. Table D.1 indicates that even if organic carbon were totally conserved, other sources must supply 12000 kg each year and, allowing for carbon losses to atmosphere, this figure would be much greater. Thus the supply of organic carbon to the loch from the leachate is insignificant.

2.2.2. CHEMICALLY DEPOSITED SOLIDS

The suspended solids content of the leachate going to Kinghorn Loch is likely to be a mixture of red mud solids flushed from the tip and material which is formed by the reaction of hard water with caustic leachate. The latter material tends to be lighter, paler in colour and more readily swept from the settlement pond. Samples of the suspended solids have been obtained at intervals over the term of the study and analysed to determine their origin. Metals were digested by boiling the sample, previously made to 2% with nitric acid, prior to analysis by atomic absorption spectroscopy while carbon was determined directly on an elemental analyser (see Chapter 9.3 for methodology). Table 2.6 tabulates these results.

date	Ca	Mg	Al	Fe	As	V	organic C	inorganic C
1-12-82	32	.64	.81	.32	...	...	4.01	11.1
9- 1-83	33.6	.41	.73	.41	.068	.031	3.59	10.6
20- 2-83	32.3	.46	.68	.28	.074	.053	3.59	10.4
14- 4-83	34	.55	.86	.31	.072	.026	3.8	11.1

TABLE 2.6. Analysis of leachate suspended solids. Results are given in % (dry weight).

The high level of calcium in these samples indicated that 80-85% of the solids was calcium carbonate. Aluminium and magnesium were probably associated with about 4% of clay minerals while the iron may represent hydrated iron oxide at about 0.5%. It is evident that this material is derived primarily from precipitated reaction products and is not red mud solids. On subjecting the solids to X-ray diffraction crystallography it was found to contain calcite and a little quartz along with broad amorphous baseline material.

2.2.3. RED MUD

Bulk composition data are readily available for red mud and Table 2.7 sets out a comparison of the ranges found in the literature for red muds generated from bauxites originating in Guyana[7], Australia[1], Greece (and elsewhere)[12], Jamaica and Brazil[13]. These are compared with information supplied by BA Chemicals Ltd for 1974 (I) and 1978 (II) and analysis (one sample only) carried out during the present study.

	All references		BA Chemicals		present study
	range	approx. mean	(I)	(II)	
Al_2O_3	4-40	15	17.9	15.8	19.9
Fe_2O_3	8-80	45	48.4	51.0	38.8
SiO_2	3-20	10	3.9	5.9	12.6
Na_2O	1.5-11	4	5.6	6.9	6.7
TiO_2	0-20	5	6.8	7.6	4.9
CaO	0.7-20	4	3.5	2.0	6.1
L.O.I	5-20	10	13.9	10.7	10.6
MgO					<.001
K_2O					.007
MnO					.002
P_2O_5					.254
C(inorg)					.69
C(org)					.05

TABLE 2.7. Composition of Red Mud from Whinnyhall Tip - Comparison with literature values. L.O.I. = loss on ignition. All values as % dry weight.

It will be noted that the analysis shows the red mud to be of typical average composition though the soda content is somewhat high. This is also reflected in the pH of the extracted liquor. Red muds generally fall within the range pH 11.6-12.8 whereas that from Whinnyhall Tip is higher at pH 12.8-13.5. The calcium content, though in some small part derived from calcite or dolomite in the bauxite, mainly originates from the liming of mud during separation.

The inorganic carbon figure indicates that less than half of the calcium is present as carbonate, some 5.8% of the mud being carbonate (as calcium carbonate).

At least half of the minerals found in red mud are formed during the Bayer process[13], goethite (FeOOH) being the principle mineral to remain unaltered. However X-ray diffraction studies, carried out on my behalf by the University of Strathclyde Department of Applied Geology, found that the hydrated iron oxide phase of red mud taken from Whinnyhall Tip consisted of hematite with only a minor goethite component.

Orban et al[14] have dealt with the passage of bauxite through the process and determined the mineralogy of the altered products. The minerals that are formed (or remain unaltered) is a function of the calcite and dolomite content of the bauxite. As the bauxite used at Burntisland is generally of very low total calcium content (typically 0.2% as CaO) it is sufficient to consider only low calcium processes. The first minerals formed involving calcium and magnesium are titanates $CaTiO_3$ and $MgTiO_3$ but as the liquors are inadequate to complete this reaction, other minerals of the type $Na_2O.3TiO_2$ and Ca(Mg,Al,Fe) titanates will form. In low calcium bauxites of this nature the residual aluminium would be restricted in the range of minerals it could form and most would be incorporated in sodalites (sodium aluminium hydrosilicates). Some residual boehmite and diaspore (hydrated aluminium oxides) would remain unaltered and an appreciable amount may be incorporated in the surface of iron oxides and calcite. Sodalites formed may typically be represented by

$3(Na_2O.Al_2O_3.2SiO_2).Na_2CO_3.2H_2O$ and $3(Na_2O.Al_2O_3.2SiO_2).Na_2SO_4.2H_2O$. The formation of these minerals would also account for the loss of sodium ions during the process and their presence provides the red mud with a high ion exchange capacity. Some of this capacity will be used by calcium during the subsequent liming to form calcium aluminium silicates and calcite and the surface of calcite particles so formed are found to become adulterated by hydrosilcates and titanates of Ca, Mg, Al and Fe[14].

Red muds are materials of high porosity and large specific surface[13] (typically 22-36 $m^2\ g^{-1}$ for this type of bauxite) and the sodalites formed tend to be microcrystalline (0.1-1um in diameter). These physical characteristics and the high base exchange capacity (500-1000 $mEq\ kg^{-1}$) of red mud means that the removal of sodium causticity from the tipped material will present a long-term problem but also that any fresh red mud entering Kinghorn Loch will possess a high metals scavenging potential. Sodium is likely to be replaced initially by calcium and hydrated iron oxide surfaces will attract arsenic.

It will be realised from Chapter 2.2.2. that red mud was not normally brought into the loch as suspended matter. However when the contents of the settlement pond were released into the loch the flood debris certainly contained a considerable proportion of red mud, apparent by its bright red colour. The aqueous inputs to the loch contained virtually no iron and yet, despite the high sedimentation rate within the loch, the sediment column contained around 2.5% iron (as Fe). Suspended solids entering the loch, given the approximate sedimentation rate from Chapter 2.1, would provide only enough iron to give

the sediment a level of 0.02% iron, and detrital inputs from elsewhere cannot make up this difference. Thus a substantial quantity of red mud must have been finding its way into Kinghorn Loch. This input of iron is of great importance for the understanding of the processes occuring as will be seen during later discussion.

2.2.4. BURNT BLAES

Burnt blaes is a material that was dumped at the west end of the Whinnyhall Tip "valley" during the nineteenth century as the waste from the oil shale distillation industry that developed in the area. Oil shale was mined from beneath Whinnyhall and indeed Kinghorn Loch. The industry had declined by 1910. Burnt blaes was subsequently used in enclosing the red mud tipping site and is much in evidence at the west end of Kinghorn Loch. The blaes is composed of burnt siliceous shale which forms hard, though brittle, lumps. It appears to be chemically inert. Consequently, in the context of this study, blaes is not thought to be of significance.

CHAPTER THREE

ORIGIN AND CHEMICAL COMPOSITION OF NATIVE WATERS

3.1. ORIGIN

3.1.1. PHYSICAL FEATURES

The topography of the catchment areas of the streams serving Kinghorn Loch is quite inspiring. Allan and Knox[15] in 1934 described it thus, and quote:

> "Thus, where the Calceriferous Sandstone volcanic rocks outcrop around Burntisland the ground rises rapidly from the coast to a height of over 500ft [150 m] in a series of craggy escarpments with north-facing dip-slopes. Projecting above the general level of the volcanic rocks and associated sediments are a number of isolated hills marking the sites of volcanic vents; the most prominent of these being The Binn of Burntisland, 632ft [193m] and Dunearn Hill, 727ft [221m]"

Where each north dipping scarp outcrops, a narrow, shallow valley is formed which runs gently eastwards. The catchment of Glassmount Reservoir is one of these (see Figure 1.1.) as is that which feeds into Whinnyhall Tip. The very shallow valley in which the tip sits also feeds eastwards with a sharp scarp to the north and a sharp scarp falling away to the Kirkton Burn on the south. Rock outcrops extensively in the area and all the valleys are covered, probably to quite a shallow depth, with glacial deposits. Reference to Figure 3.1. will show that the catchment areas referred to as "Glassmount Reservoir" and "Kinghorn Loch" in Figure 1.1 are contained entirely on the basalt and basaltic tuff that overlies the Oil-Shale Group of the Calciferous Sandstone Series of the Carboniferous Period. These olivine basalts were studied by Allan[16] who divided the basalt flows into three types shown in Figure 3.2. The three types were described in the following manner:

1. Dalmeny Type. A rock with many small phenocrysts of olivine and few of augite and felspar in a fine-grained, non-ophitic groundmass of felspar laths and granular augite.
2. Hillhouse Type. A rock similar to the Dalmeny type basalts, but with a groundmass containing much more augite than felspar, usually with some residual glass. The augite shows zoning, hour-glass structure, and twinning.

FIGURE 3.1. Solid geology of the catchments

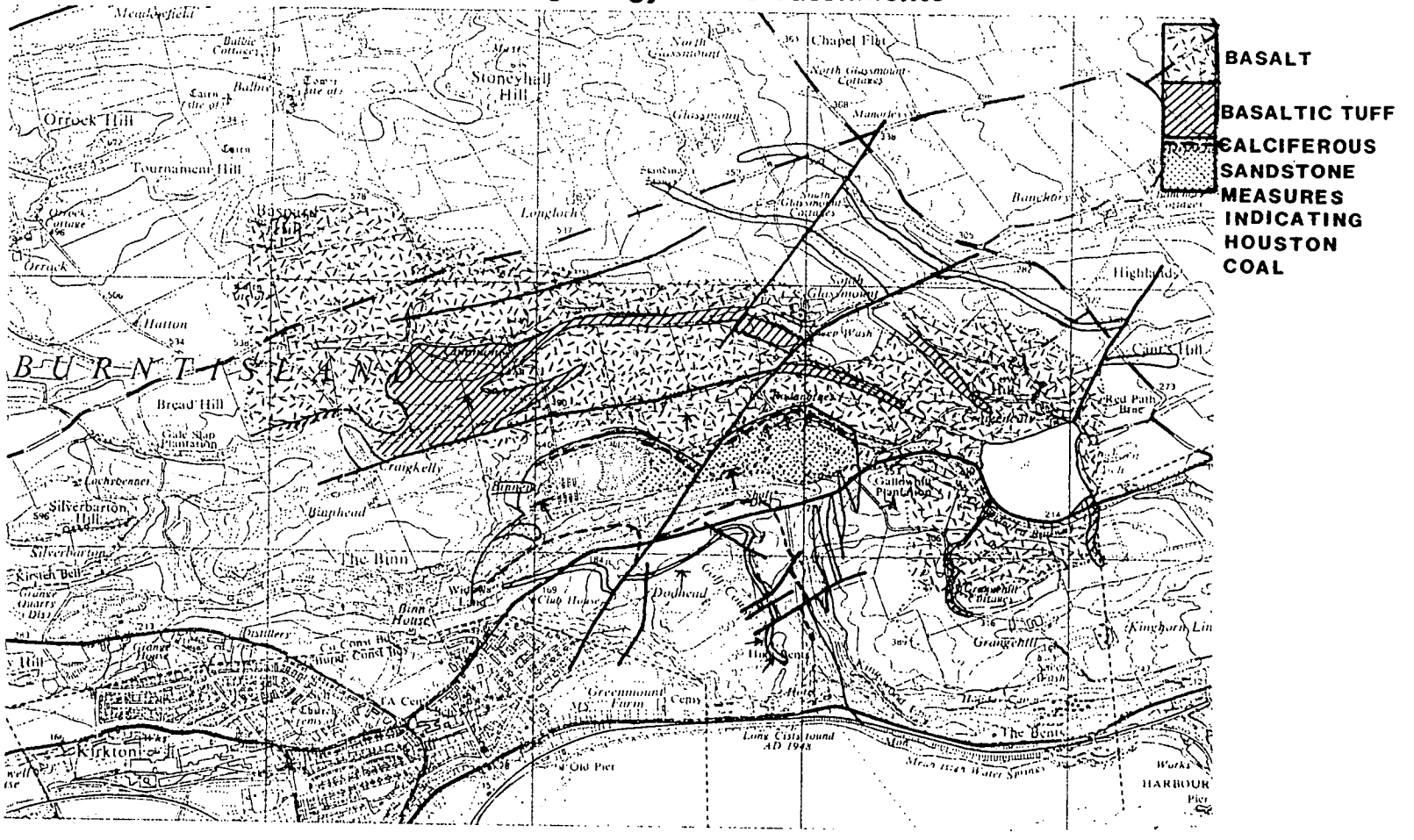
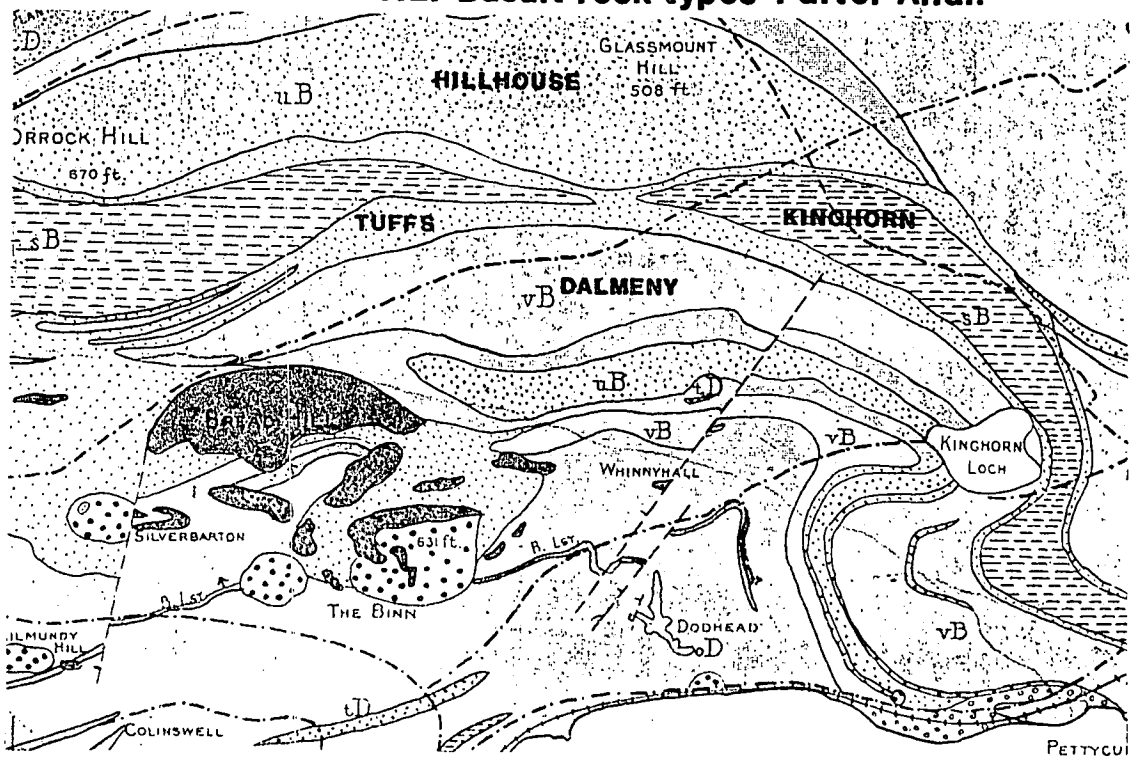


FIGURE 3.2. Basalt rock types : after Allan [16]



3.Kinghorn Type. A rock carrying many phenocrysts of olivine and augite in nearly equal proportions. The pyroxene, which is in slightly smaller crystals than the olivine, is somewhat purplish, and has a strong tendency to glomeroporphyritic aggregation. The groundmass is dark and fine-grained, consisting of laths of felspar, granules of augite, sometimes a little olivine, and specks of black iron oxide, together with a considerable quantity of uncrystallised base.

Elemental analysis of the types is also given, and reproduced here as Table 3.1. It will be noted that all are very similar in chemical composition.

	Dalmeny	Hillhouse	Kinghorn
SiO2	46.28	42.49	43.56
Al2O3	14.18	13.85	13.77
Fe2O3	11.13	11.91	12.01
MgO	10.82	11.21	10.81
CaO	9.88	9.76	10.00
Na2O	2.58	2.39	2.72
K2O	1.01	0.87	0.46
TiO2	2.06	2.51	2.85
P2O5	0.44	0.61	0.27
MnO	0.09	0.29	0.24

TABLE 3.1. Elemental Analysis of Basalt Rock Types. (analysis of Dalmeny type actually labelled Craiglockhart type - a similar rock.) Analysis is in % of gross weight.

Allan found that the tuffs contained not only volcanic material but dark shale, sandstones, thin limestone and coal, similar in diversity to those occuring below the lavas.

Whinnyhall Tip and the Kirkton Burn lie below the base of the lava. The scarp, forming the north edge of the tip, is topped by lavas lying over 4 m of sandstone with a coal seam, the Houston Coal, at its base. This coal seam was less than 0.5m thick and consisted of inferior coal containing much pyrite. The sandstone has a thickness of some 40 m above the Fells limestone and underlies Whinnyhall

Tip[15]. It is said to be of inferior quality, being soft and friable and containing silt and mudstones. It was used as an aquifer for public supply prior to becoming polluted and was believed to be artesian. Some 90 m below the lava base are the Dunnet Shale beds from which oil was extracted.

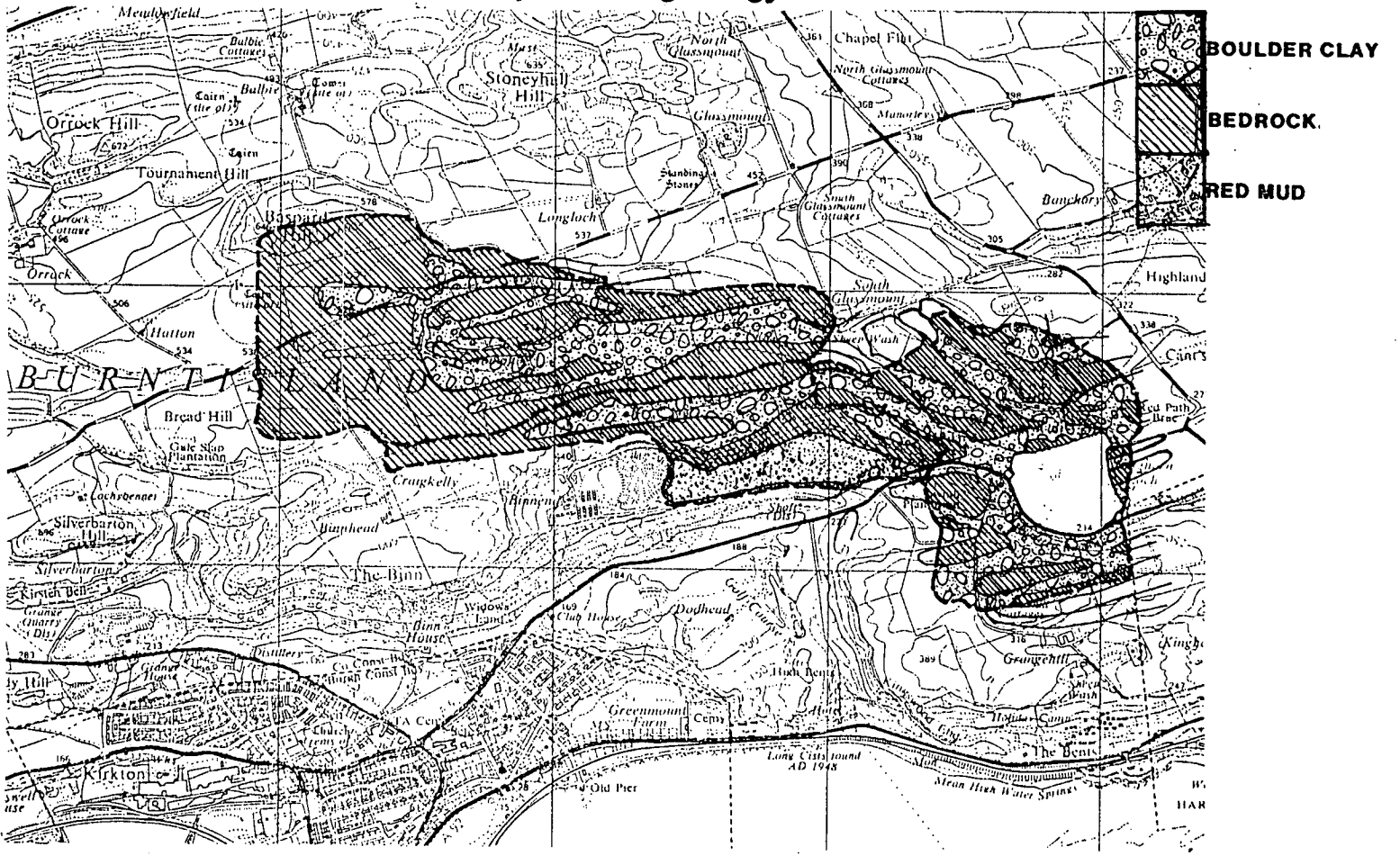
Figure 3.3. shows the superficial geology of the area. The boulder clay situated on the volcanic rocks are stiff clays containing many boulders and are rusty brown in colour[15]. Several of the hollows contained kettle holes and these are filled with peat. Boulder clay also overlay the sandstones of Whinnyhall Tip. This hollow held a lake and its section, as seen in 1887 during the railway construction, consisted of 0.3m peat, 0.3m marl, 1m greenish clay with shells, and 0.3m clay without shells over boulder clay[15]. It is probable that the construction of this cutting diverted drainage of the natural waters of Whinnyhall Tip from Kirkton Burn to Kinghorn Loch.

3.1.2. DRAINAGE PATTERN

In Figure 1.1. drainage to the loch had been divided into three "catchments" - Whinnyhall Tip, Glassmount Reservoir, and Kinghorn Loch. This is because of the special considerations required in considering flows from Whinnyhall Tip and because the water obtained via Glassmount Reservoir has been intercepted from its natural course.

If we assume that the area of Whinnyhall Tip that drains to Kinghorn Loch is 0.05 km^2 then:

FIGURE 3.3. Superficial geology of the catchments



For average annual rainfall(ex.Meteorological Office)= 750 mm

For mean evapotranspiration(ex MAFF Bulletin No.16) = 470 mm

For loss to groundwater through boulder clay; say = 50 mm

Then volume of run off =0.36 l s^{-1}

In fact the flow was 2.73 l s^{-1} for 1981 to 1983.

Thus this simple treatment is inadequate. It is probable that the drainage from the whole of the valley goes to Kinghorn Loch and that the leachate to the Kirkton Burn acts as an overflow carrying drainage from above the consolidated red mud. Thus the loch would receive drainage from as far as Binnend at the head of the valley but not necessarily its fair share from the tipped red mud. Seepage to groundwater is likely to be much greater at Binnend where there is little boulder clay. Further although there may be losses by evaporation there is unlikely to be any through transpiration over much of the tip area. It is not considered that the red mud itself will in a net way contribute significantly to any flows. The situation is further complicated by the fact that much of the water draining this valley is spring water issuing from a line of springs at the base of the basalt. By consideration of the relative level of sodium (as a conservative parameter) in the red mud interstitial water, native water [taken from Craigencalt Farm (North) inlet analysis] and rainwater compared to that in the leachate, it is possible to estimate that the red mud interstitial water is diluted approximately 5:1 by native water and rainwater in forming the leachate.

When the loch was surveyed in 1905 as part of the Royal Geographical Survey[17] the catchment area was stated as being less than 60 ha, a ratio of only 5:1 compared to the surface area of the loch. Apart from some channelling of the marshy ground at the north west end of

the loch and a wet area to the west of the main Craigencalt Farm (North) inlet there are no obvious flows into the loch within its own natural catchment.

Glassmount Reservoir collects water from an extensive series of underground culverts draining the area due west of the reservoir as far as Baspard Hill. The full extent of this collector system is not known but from the number of known springs in the area it is reasonable to assume that a significant proportion of the water going to the reservoir is derived from the basaltic tuff aquifers extensively outcropping in the area. In fact if a similar calculation to that given above is applied to a calculation of likely flow passing the mill at Craigencalt Farm then, for a catchment area of 1.4 km^2, the mean flow would be 9.9 l s^{-1}. This compares with an actual flow of 15±2.7 l s^{-1} for 1981-1983. The precision available for the calculated value is not known. The evapotranspiration in the area is unlikely to be typically average and indeed is likely to be below average due to the lack of tree cover. The estimated contribution from groundwater loss is based on a layer of average boulder clay which presents a considerable resistance to hydraulic transfer. Much of the catchment valley floor is on permeable tuff which contains several springs. If springs can rise in this area then it is likely that discrete pathways exist for water to sink as well. If it is assumed that evapotranspiration could be 20% lower and that the variance in groundwater losses could be ±100% then the precision of the estimate becomes 10.8±3.1 l s^{-1} (95% c.l.). Thus it is probable that at least 25% of the flow past the farm will have originated as groundwater.

Agricultural development of this catchment is greater than in the other catchment areas involved. Even so the majority of the area is given over to enclosed pasture and rough grazing with a smaller contribution from arable and animal feedstock production. It is unusual that this reservoir has consistently produced water with a high nitrate level (up to 10 mg l^{-1} as N) and this problem finally led to its use being discontinued in 1975. It was brought back into use in 1980 for a short time but at all other times full flow has been entering the loch (mean flow for 1981 to 1983 was 15 l s^{-1}). Problems with high nitrate levels are known, by the Water Supply Services of Fife Regional Council, to arise in areas of high aquifer production. The reason for this is not known.

The water flowing from this small reservoir is culverted to a filter house and thence to a mill pond serving the disused mill at Craigencalt Farm. It passes down the mill race into the loch.

3.2. CHEMICAL COMPOSITION.

Samples of the native water inputs to the loch have been collected and analysed on a weekly basis from January 1st 1981 until 1984. The data have been conveniently divided into pre- and post-May 1983; the time when the leachate flow was removed from the loch. Prior to this time the only discrete unpolluted native water input was the north inlet past Craigencalt Farm and the analysis is collated in Table A.2. of Appendix A.3. By reference to the statistical appraisal given in Appendix A it will be seen that for all important parameters (other than phosphate which is very low anyway) the requirement for the long-term mean to be within 10% of the true figure is met for concentration measurement but only at 20% for loadings (at 95% c.l.).

After May 1983 the flow at the settlement pond dam decreased but did not cease due to the flow from a natural spring at the head of the cutting. The water flowing from the settlement pond was redesignated as the west inlet. Post-May 1983 samples of the north inlet are collated in Table A.3. and of the west inlet in Table A.4. of Appendix A.3.

The north inlet possesses an unusually high pH for an oligotrophic water, averaging 8.1. pH's in excess of 8 would normally only be met, in the United Kingdom, by productive waters. The water is also moderately high in dissolved silicon (that which passes a 0.1um membrane) averaging 4.3 mg l^{-1} as Si. It is this input in particular which allows an interest in clay or aluminosilicate synthesis in the loch as the leachate, which is high in aluminium, is deficient in silicon. Due to the mode of collection of the north inlet water and its retention by Glassmount Reservoir, the inlet makes only a minor contribution to the suspended load to and within the loch. This is estimated (from Table A.2) at 5000 kg detrital solids each year.

No reliable information appears to be available concerning the composition of the water from the springs lying beneath the red mud. Those analyses that are available are, in the main, incomplete and apparently inconsistent and, excepting one from 1958, have not been considered here. However data are available from the author's study of the Kirkton Burn catchment between 1977 and 1979, carried out in pursuance of his normal duties with the F.R.P.B. These data are illustrated in Table 3.2. and include analyses of the source of the Kirkton Burn and several native springs draining to the Kirkton Burn within 0.5 km of its source.

location	I	II	III	IV	V
pH	7.5	8.3	8.5	7.2	.....
calcium	212	213	177	224	189*
magnesium	66	62	47	50	19*
sodium	184	144	85	96	108
potassium	9.6	20	13	12	.....
iron	.17*	.63*	.08*	11.8*	2.8*
manganese	.004	.205	.024	.237	.....
zinc	<.001	.003	.005	.004	.....
nickel	.002	.011	.004	.009	.....
copper	<.001	<.001	<.001	<.001	.....
chromium	.009	.005	.008	.012	.....
lead	.013	.015	.010	.004	.....
cadmium	.002	.002	.003	.005	.....
vanadium	.3	<.1	<.1	<.1	.....
aluminium	<.1	.1	.2	.2	2.6*
arsenic	.06	<.005	<.005	<.005	.....
alkalinity ($as CaCO_3$)	390	210	290	270	6.5@
hardness ($as CaCO_3$)	.....	.....	.....	.....	645*
chloride	55	36	26	27	33
sulphate (as S)	126	.....	.....	.....	130
nitrate (as N)	.15	.....	.....	.....	.....
ammonia (as N)	.8	.....	.....	.....	.....
phosphate (as P)	<.002	.....	.....	.....	.....
silica (as Si)	.....	.....	.....	.....	3.3*

TABLE 3.2. Analysis of Springs Rising Within the Calciferous Sandstone Series.
I rising of the Kirkton Burn
II water collected by pipe 100m downstream of I
III spring water entering burn 150m downstream of I
IV ferruginous spring water entering burn 300m downstream of I
V analysis of spring water from Whinnyhall Tip ex.oilshale workings (BA Chemicals - 1958).
All results in mg/l dissolved determinand other than marked * for total determinand. @ is considered an erroneous result.

All of these risings probably exit from mine workings within the Dunnet Shale beds but should be reasonably typical of the water contained within the Calciferous Sandstone Series proper. The west inlet to the loch originates from a similar source but may be affected to some extent by leachate seeping through the wall of

Whinnyhall Tip and also by the sediments still in the settlement pond. Vanadium and arsenic levels found in the Kirkton Burn rising indicate that it too was polluted by seepage from Whinnyhall Tip. It will be noted that the analysis of a spring, now buried by the tip, performed by BA Chemicals Ltd in 1958, is of a high sulphate, high calcium and moderate sodium and chloride type water similar to the other sources shown. However the alkalinity of this sample appears erroneous and no pH is provided. These waters are considerably more mineral-rich than the north inlet to Kinghorn Loch, though of a similar type. Thus the ratio of native water:leachate leaving Whinnyhall Tip of 5:1, as previously postulated on the basis of north inlet water analysis, may be an underestimate of the dilution available. The Kirkton Burn rising shows a much lower nitrogen status than the north inlet. Apart from the west inlet spring however, seepage to the loch from non-discrete sources would come off the basalt bedrock or its derived boulder clay and would therefore be expected to have a composition similar to that of the north inlet.

CHAPTER FOUR

KINGHORN LOCH
AQUEOUS CHEMICAL COMPOSITION
AND ESTIMATION OF LOSSES
TO THE SEDIMENT

4.1. PHYSICAL DESCRIPTION.

Kinghorn Loch is set in a hollow in the basalt bedrock. It is probably underlain by boulder clay although bedrock is exposed along its east and north shores and is close by the south and south-west shores. The north shore is virtually devoid of trees and only a few occur along the east. The shore bordering the Kinghorn to Burntisland road is planted with trees along its length as is the west end which consists of brush and shallow water fronted by a line of dead trees set in the water. The level of the loch was raised in the nineteenth century by the construction of a dam and sluice at the outlet, drowning small parcels of land at the west end behind the dead trees and forming the bay at the point where the north inlet enters the loch. The level was further raised in the 1970's but as this caused flooding of the road the original level was restored.

Figure 4.1. shows a plan of the loch with the sampling station notation superimposed upon it. The sampling grid allows 51 sampling points at 40-60 m intervals and this number was chosen as the largest practical, in order to allow a statistical appraisal of the invertebrate numbers for the 42 sampling points within the body of the loch proper. Permanent onshore features were used as markers for these trancepts wherever possible. Wooden stakes were driven into the ground to within 25 mm of ground-level to mark all other trancepts, with one peg near the shore and another approximately 20 m in trancept line behind it on the hillside. On the east shore this permanent marking was not possible and the remote pegs required removal each Autumn prior to ploughing of this field. The pegs were positioned by use of a theodolite and checked for line by compass to be within 0.009 rad (30') of the desired bearing.

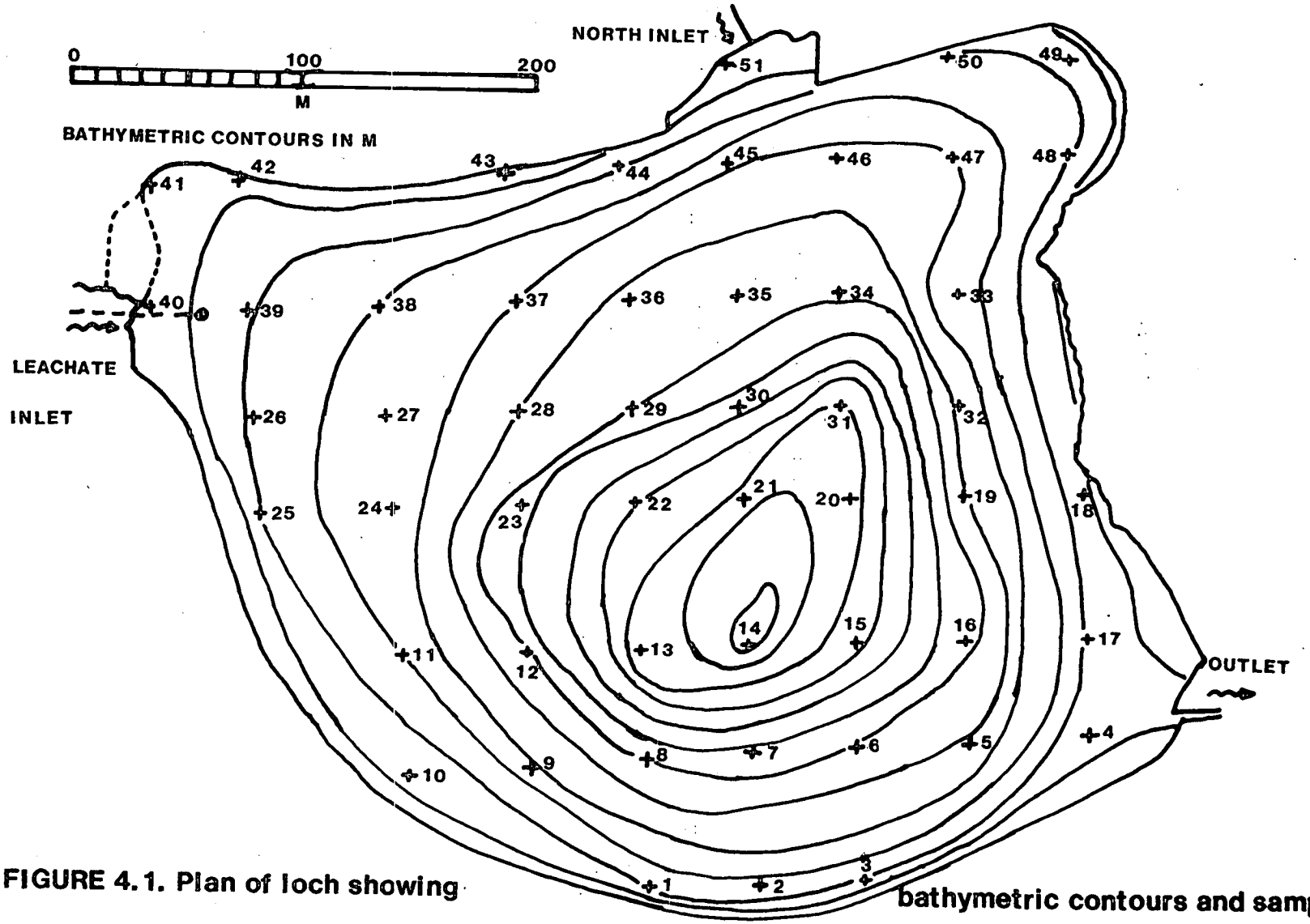


FIGURE 4.1. Plan of loch showing bathymetric contours and sampling stations.

Initially, bouys, which were positioned on the loch by the yachting club, were used to aid trancept location but these were driven off station by strong winds. In consultation with the clubs involved properly anchored buoys were placed in position but these were cut adrift by persons unknown. Similar problems were experienced with the pegs being removed (despite being 0.5 m in length and inserted with a sledge hammer) and continual remedial work was required. Eventually any attempt to use water-based markers was abandoned.

When surveys were conducted, land-survey poles were carefully positioned against the rear of the pegs in order to locate the trancepts from the boat. The accurate positioning of these poles was critical for the correct location of sampling positions on the loch. It is estimated that location of the far (that is south- and west-most) positions was within ±5 m. Several surveys of the loch were carried out, for various purposes, during the period of study. On each occasion a boat was provided by the Estuary Survey Section of the F.R.P.B.; variously a 17ft Dory, Task Force or 12ft inflatable craft fitted with outboard motor.

The initial survey of Kinghorn Loch consisted of a bathymetric profile and the taking of samples for particle size analysis. An attempt was made to use an echo sounder for depth measurements but this proved unreliable due to the incoherent nature of much of the bottom sediment surface. A flat weight on a marked line was used in its stead and Figure 4.1. charts the profile obtained. The maximum depth of the loch proved to be 12.8 m at a point to the south of the geometric centre of the loch. 50% of the area lay at a depth in excess of 4.2 m whilst 50% of the water volume lay below 2.5 m.

Figure 4.2. illustrates the accumulated volume of the loch and shows that a normal summer draw down via the penstock by 1.4 m reduces the water volume to 70% of capacity. Figure 4.3 illustrates water levels found in the loch during the period of study and shows that the loch was not drawn any further than this, although previously extra draw down has been accomplished by pumping over the spillway. Exceptionally, in 1976, the loch surface was drawn down by 4.3 m indicating a reduction to 27% of capacity and exposing 50% of the bottom sediments.

4.2. DEVELOPMENT OF THE POLLUTED STATE.

The natural chemistry of Kinghorn Loch would be that of the north inlet waters. The loch should be phosphorus deficient and thereby oligotrophic. Over a period from the mid-1970's up until May 1983 the loch regularly suffered from excessive phytoplanktonic activity at a level seen in very few water bodies in this country. Additionally, the mean pH of 9.94 was prohibitively high for the survival of fish and most invertebrates. The loch had the dubious distinction of possessing by far the highest level of dissolved arsenic of any waterbody in the United Kingdom[18], a level of 500 ug l^{-1} as against a level in most waters of less than 5 ug l^{-1}. Figure 4.4. charts the pH of the loch over the period 1954 to 1985 and vividly illustrates the onset of significant pollution in 1961 and the ever increasing pH up until the removal of the leachate. It also shows the surprising rapidity of the improvement in water quality that followed. Pre-1981 data for compiling this figure were obtained from F.R.P.B. records and from BA Chemicals Ltd.

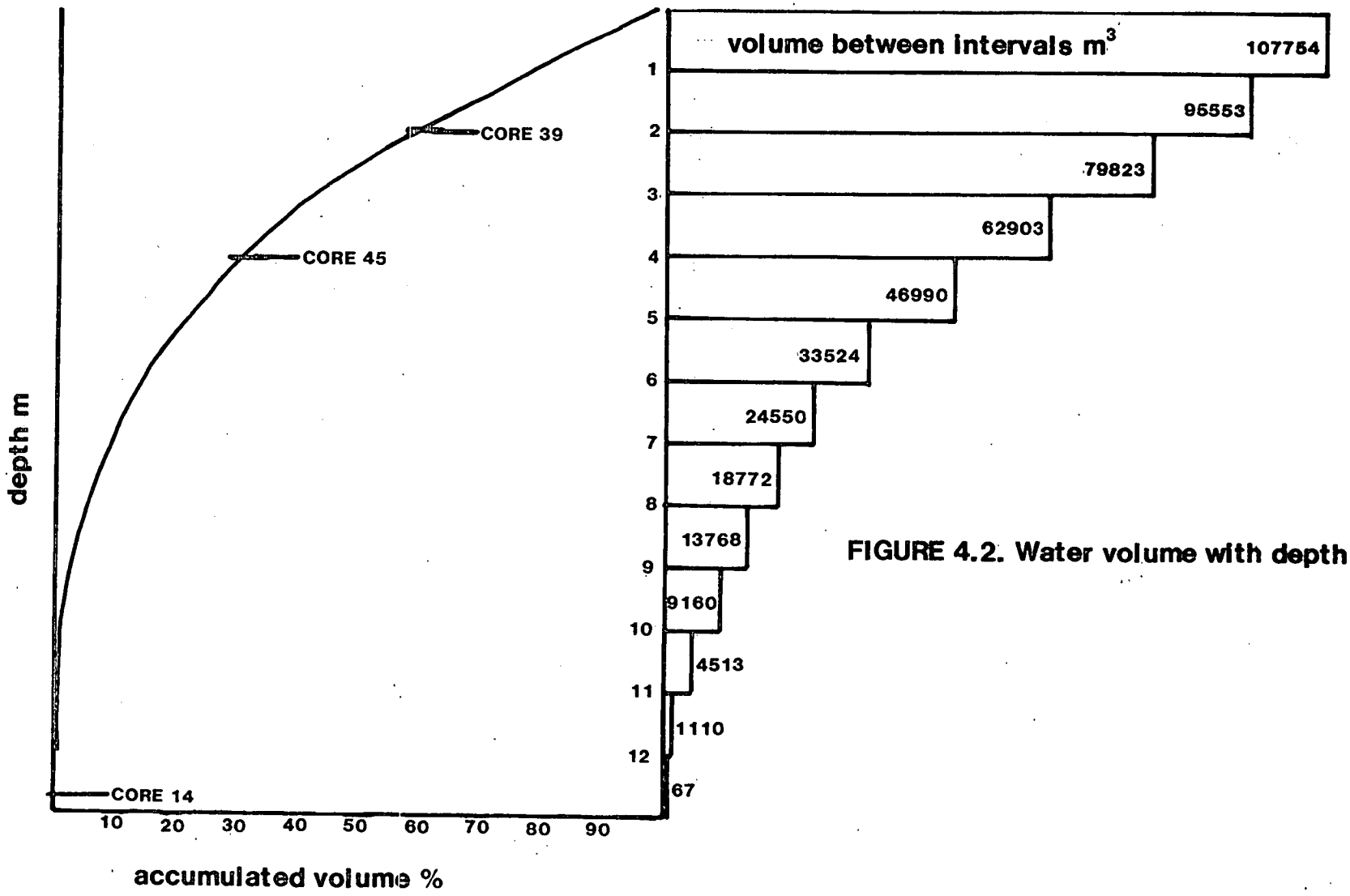


FIGURE 4.2. Water volume with depth

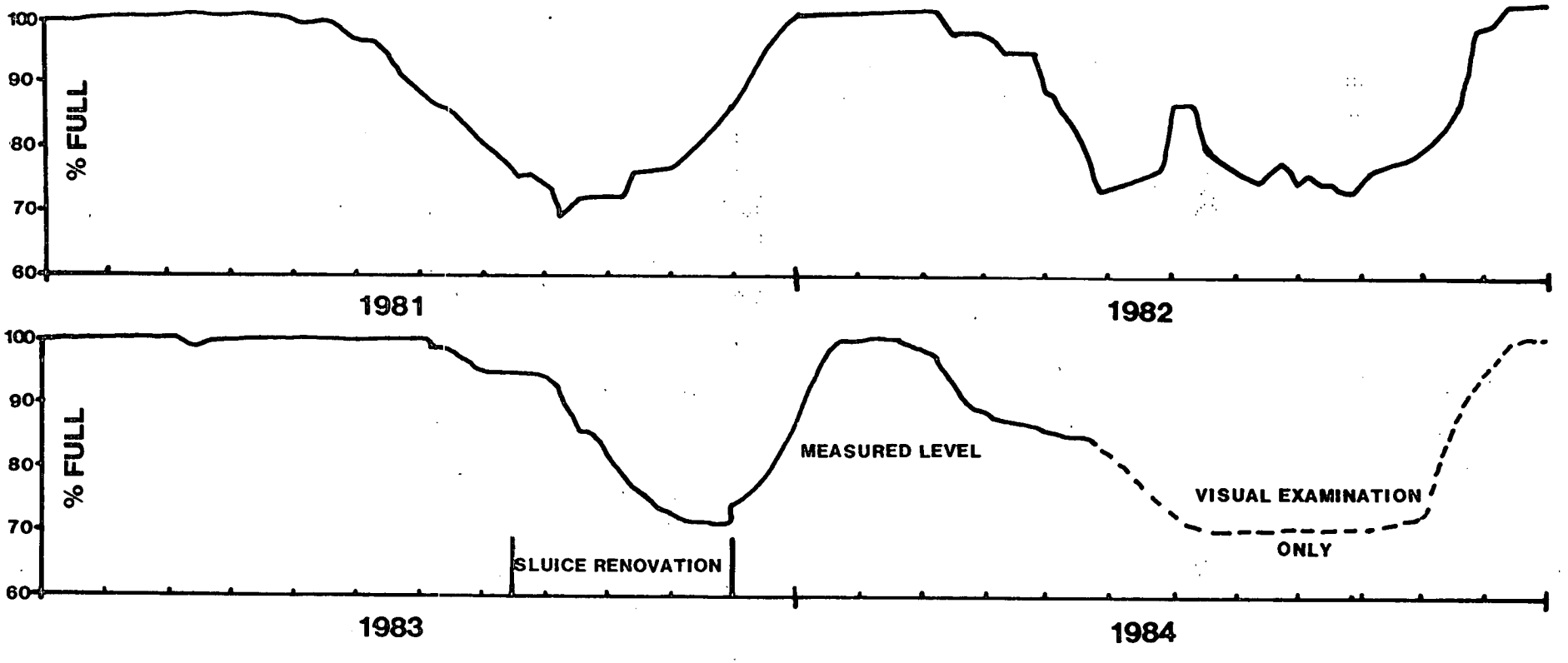


FIGURE 4.3. Water level

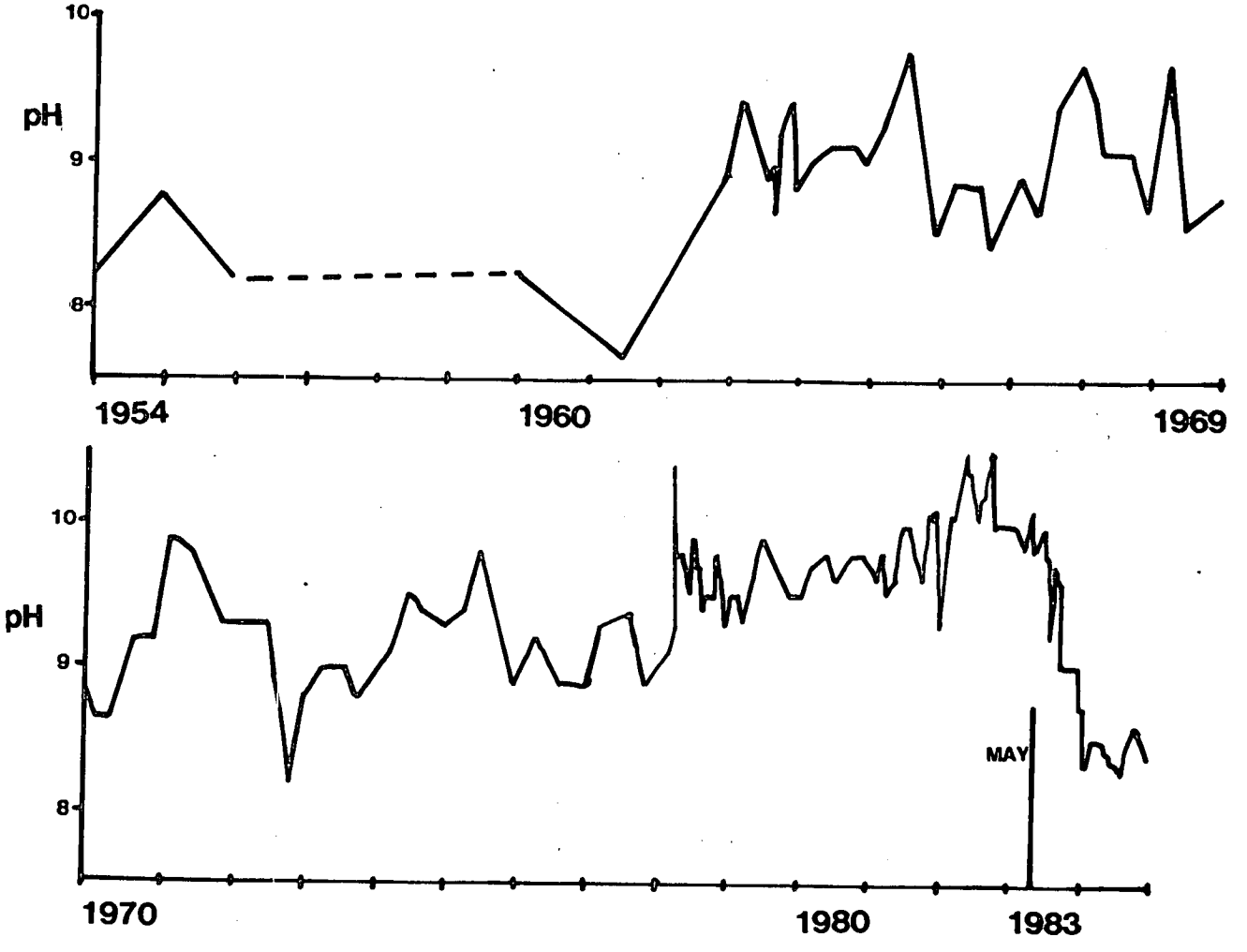


FIGURE 4.4. pH of Kinghorn Loch at outlet

4.3. CHEMICAL COMPOSITION.

Table A.5. of Appendix A.3 collates data for the analysis of the loch over the period up to May 1983 and Table A.6. illustrates its subsequent recovery. The data contained in these tables were obtained from a sampling station near the outlet and need not be representative of the water body as a whole. The loch is relatively deep for its size and may be expected to be thermally and chemically stratified. Several surveys were carried out during calm weather, between February and October 1981 in order to ascertain whether any such stratification would occur and to estimate the homogeneity of mixing and chemical reaction throughout the loch. The results of these surveys, each covering a three dimensional grid of up to 48 samples, are displayed in Tables A.7. to A.11. of Appendix A.3. These surveys include two taken during prolonged calm weather in October. It is evident that the chemistry of the loch water was surprisingly homogeneous over three dimensions. Given this general observation, station 39, which will be seen from Figure 4.1. to be close to where the pipe carrying the leachate entered, showed a very slightly elevated causticity, although on one occasion this station showed pH 11.1, 1.2 pH units above loch mean. Similarly a slight elevation of calcium level is indicated within the bay of the north inlet. These effects are marginal and the transition into general loch body chemistry is rapid.

Of more interest however, though again of very local effect, are the reductive and re-solution processes that evidently occur at or near the mud-water interface of the deeper stations. The situation is characterised by low dissolved oxygen saturation and high electrical conductivity, dissolved calcium, magnesium, aluminium and iron,

elevated alkalinity and the presence of free sulphide. Unfortunately arsenic was not determined for these surveys. These processes have only been observed very locally and disappear rapidly within the body of the loch water. Reductive processes within the sediment will be discussed in Chapter 5.

The chemical surveys were supplemented on other occasions over this period by the instrumental measurement of temperature and dissolved oxygen down the profile of station 21 and the findings are summarised in Figure 4.5. It is evident that, although thermal stratification did not occur to any significant extent, in calm weather the mud-water interface was often anoxic. The summer of 1981 proved to be a time of relatively low phytoplanktonic activity (see Figure 7.5) and the data should be compared with those for July 1983 (see Figure 4.6) when extremely high phytoplanktonic activity was observed. The figure shows that on 10th July 1983 the loch was thermally stratified and that the high phytoplankton content of the upper waters was having a dramatic effect on the dissolved oxygen profile below 2 m to the extent that the mud-water interface was anoxic. The pH profile showed little variation with depth. This day was completely taken up with the taking of sediment cores by divers of Fife Sub-Aqua Club and so no further investigations were possible. Unfortunately the calm weather had broken before a boat was available for more intensive sampling of the anoxic zone.

The reductive processes appeared to occur only locally within the water body itself and any metals taken into solution were redeposited. Arsenic may however be lost to the atmosphere either as arsine or organoarsenicals (see Chapter 4.7.6). Overall, these

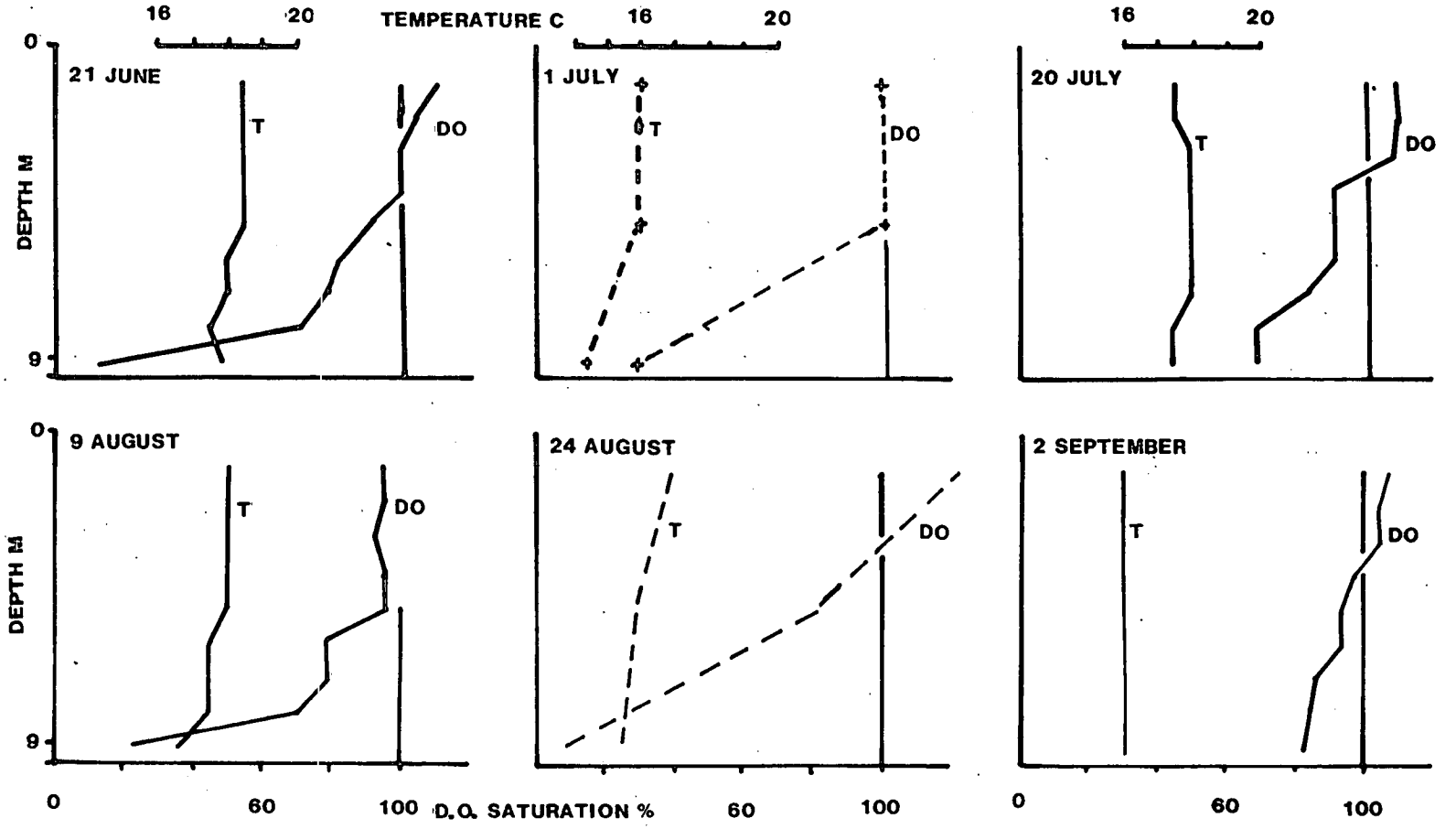


FIGURE 4.5. Daytime temperature and oxygen profiles for Station 21 (June - September 1981)

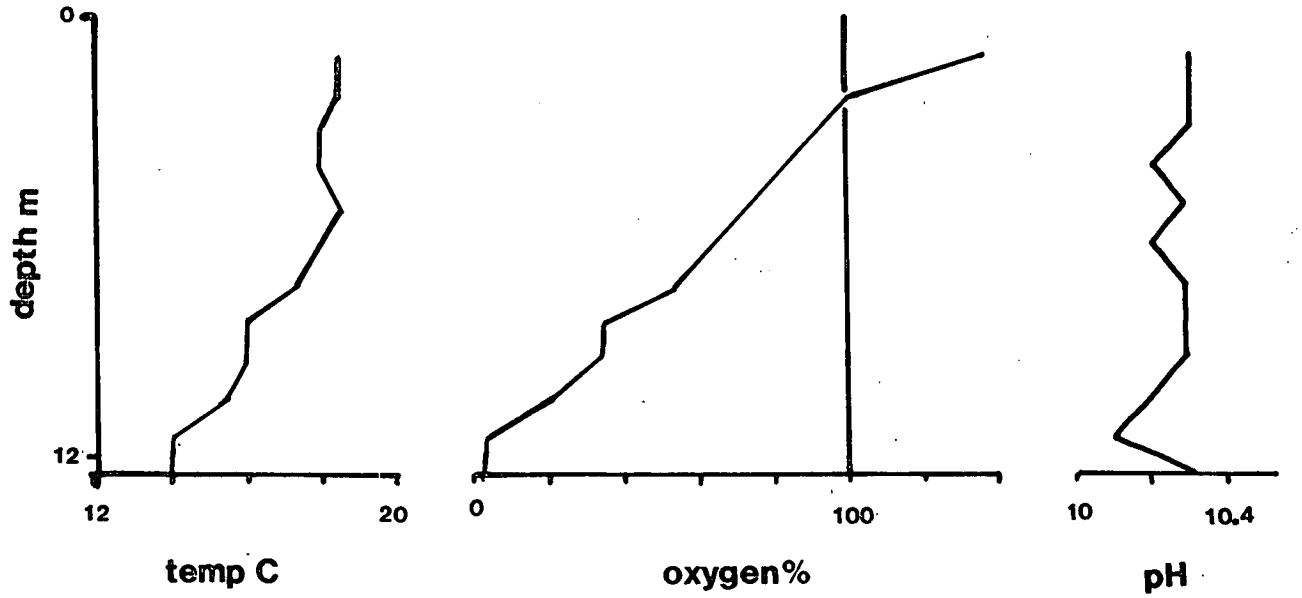


FIGURE 4.6. Daytime profiles for Station 14 , July 10, 1983

processes will have had only a minor effect in determining the gross deposition rate. They do however indicate likely conditions within the sediments and are therefore of vital interest in determining the broader relationships within the whole water body-sediment system.

The concentration of determinands found in the loch were affected by two major processes both of which caused irretrievable loss of material to the sediments. The first process was the chemical reaction of the leachate and the inlet waters to form carbonate and aluminosilicate minerals and the second was the phytoplanktonic productivity within the loch which grossly affected the nutrients present. These processes would be reflected by similar variability of related determinands with time. A significant correlation between two determinands will therefore indicate joint participation in such processes and the following section was set out to identify these relationships.

4.4. CORRELATION BETWEEN PAIRS OF DETERMINANDS.

A computer program, "KLOCHCOEFF" (see Appendix E.1) was written to provide evidence of correlation between pairs of determinands by comparing each pair of analysis results obtained for those determinands in the loch water over the period January 1981 to May 1983 (results as set out in Table A.5). The correlation assumed normal distribution for the results for each determinand and used Pearson's correlation coefficient (r_{jk}) such that for determinands j and k:

$$r_{jk} = COV_{jk}/(S_j.S_k)$$

where COV_{jk} is the covarience of j and k, and S_j is the standard deviation for j. The equation used for the calculations was the

expanded form given by Davis[19]:

$$r_{jk} = \frac{\sum_{i=1}^{n} X_{ij}X_{ik} - (\sum_{i=1}^{n} X_{ij} \sum_{i=1}^{n} X_{ik})/n}{\sqrt{\{\sum_{i=1}^{n} X_{ij}^2 - [(\sum_{i=1}^{n} X_{ij})^2/n]\}\{\sum_{i=1}^{n} X_{ik}^2 - [(\sum_{i=1}^{n} X_{ik})^2/n]\}}}$$

where X_{ij} is the ith result for determinand j and X_{ik} is the ith result for determinand k for n sets of results (n = approximately 107). The following determinands were considered for mutual correlation; temperature, pH, dissolved Ca, Mg, Na, K, Al, Fe, total As, V, dissolved alkalinity, Cl, SO_4-S, SiO_2-Si, NO_3-N, NH_3-N, F, PO_4-P, electrical conductivity, suspended solids and chlorophyll-a. Because of the logarithmic abundance of chlorophyll-a the $\log_{10}$ of the result was used[11]. Correlation was generally very poor and Table 4.1. indicates the only significant relationships found. All others were worse than 0.492 to -0.505.

determinands	coefficient
alkalinity to sodium	0.783
alkalinity to conductivity	0.731
alkalinity to pH	0.678
temperature to nitrate	-0.636
conductivity to pH	0.619
sodium to potassium	0.604
conductivity to sodium	0.544
arsenic to vanadium	0.542

TABLE 4.1. Significant correlation between analytical determinands.

Correlations between alkalinity, conductivity, pH, Na and K are to be expected and it is surprising that correlations were not very much better than those found. Chlorophyll-a was not found to be well correlated at all and no sign of correlation with essential nutrients was observed. It is possible that the inverse correlation of nitrate and temperature represented a manifestation of nutrient assimilation

in summer. The levels of As and V in the leachate do appear to be related, and the continuance of this fair relationship within the loch indicates that either no removal processes are occuring for either element or that both undergo similar precipitation or assimilation. Uncorrelated determinands that are of interest are Na and Cl (0.002), NH_3 and NO_3 (0.009), Na or K and PO_4 (0.01), As or V with Al (0.016), and log(chlorophyll-a) with temperature (-0.024), NO_3 (0.034), silica (-0.08), or PO_4 (-0.101). The level of ammonia in the loch water was probably too close to the LOD to generate meaningful correlations. The lack of correlation of Al with As or V, which are related in the leachate, serves to illustrate the very different fate of Al. It is surprising that chlorophyll-a is uncorrelated with supplies of nutrients or to temperature.

4.5. TOTAL FLOW CONTRIBUTIONS TO THE LOCH

In order to quantify the processes occuring in the loch it is first necessary to evaluate the flux of material. In order to do this an understanding of the flow budget is necessary. The flow of the leachate to Kinghorn Loch passed over a small 60° V-notch metal plate weir set in the dam of the settlement pond at grid reference NT254873. It was measured on a regular basis by reference of the depth of water above the apex of the "V", to standard charts. Flow from the north inlet at Craigencalt Farm was measured by gauge board reference at a small flume for the range of 2 l s^{-1} to 60 l s^{-1}, and by timed collection of water from the mill lade discharge pipe (grid reference NT258875) for flows <2 l s^{-1}. These points were also used for the collection of samples.

The level of the loch is controlled by a penstock which regulates

flow to the abstraction pond of the tannery of Scotblair Pelts Ltd. This penstock is capable of reducing the loch volume to 70% of capacity. The outlet from the loch was provided with a purpose built rectangular profile restrictive weir which operated over the range 5 l s^{-1} to 50 l s^{-1}. Unfortunately the gradient of the stream was slight at this point and the weir was regularly swamped due to blockages downstream. In any case the opening and closing of the penstock caused the flow to be extremely erratic and only gave a meaningful indication of daily or longer-term flow when the spillway was in operation with the penstock closed. The weir was permanently lost during the reconstruction of the penstock and dam in 1983. Regular samples of the loch water were taken from the dam, 1 m to the north of the spillway, at a water depth of 0.3 m.

The Hydrology Section of the F.R.P.B. carried out current-meter flow measurements at these sites on a regular basis in order to provide satisfactory calibration. These measurements are inherently more accurate than the routine readings and provide information suitable for determining the flow contribution to the loch from non-discrete sources. However, since the penstock operation generally controlled the flow from the loch it is only that data taken during winter months when the spillway was in operation and the penstock closed that an estimate of flow budget could be attempted. It was often difficult to know whether a reasonably stable state had been reached or whether the penstock had been operating recently. Table 4.2. lists readings taken for the period 17th November 1980 to 31st March 1981 during which time overflow conditions were maintained without penstock use.

date	leachate	north inlet	outlet
17-11-80	6.9	64.4	83.0
28-11-80	4.6	56.0	67.0
2-12-80	4.3	31.0	44.2
9-12-80	3.6	22.3	47.0
17-12-80	3.5	26.3	41.7
20- 1-81	4.1	33.2	32.9
11- 2-81	2.7	34.1	33.4
12- 3-81	8.1	46.1	66.4
17- 3-81	4.6	44.4	57.2
31- 3-81	4.3	39.4	53.5
mean	4.67	39.72	52.63
s.d.	1.624	13.21	16.06

TABLE 4.2. Flow measurements of known inputs and outputs of Kinghorn Loch in l/s. Courtesy of F.R.P.B.

Coincidentally the standard deviations for these 10 results are similar to those for the long-term means of 1.625 for the leachate and 13.142 for the north inlet. Thus the estimate of the known inputs is 44.4±8.41 l s^{-1} and for the outlet is 52.6±10.15 l s^{-1}. The overlap in these estimates (at 95% c.l.) is considerable and does not allow any reasonable estimate of the contribution from sources other than known ones. An attempt to improve this precision by using sets from all flow measurements of regular samples taken between 1981 and 1983 at times when the loch was overflowing proved to be no more precise.

Table 4.3. indicates the sodium concentrations in the inlets and outlet. Sodium can generally be considered to be a conservative parameter and so may be used as a tracer element in this instance, as sodium was so much more abundant in the leachate than in the natural waters. If the flow of leachate is taken as unity then if the combined inlets (known and unknown), other than leachate, have a mean flow of X l s^{-1} then using mean sodium concentrations over the period

1981-1983		leachate	north inlet	outlet
flow	mean	2.73111	15.2673	
	s.d.	1.64265	13.3411	
sodium	mean	2017	20.7134	249.94
	s.d.	526	3.9222	39.944

TABLE 4.3. Flow and sodium concentrations for inputs and outlet; in l s^{-1} and mg l^{-1} respectively.

1981 to May 1983 then

$$249.9 = (2017+20.71X)/X$$

so $$X = 7.71$$

Also using the standard deviations about the means for sodium levels in these waters the precision achieved at 95% c.l. would be a ratio of leachate:natural input of 1:7.71±0.46 which compares with a 1981 to 1983 annual mean of 1:5.59±0.39 from actual flow readings. The difference is significant at a 95% confidence limit. Thus at a leachate flow of 2.7 l s^{-1} and a north inlet flow of 15.3 l s^{-1}, seepage and non-discrete inputs contribute 5.5±2.3 l s^{-1} to the flow; i.e. between 19 and 45% (at 95% c.l.) of the total input flow. The mean contribution from non-discrete sources is 32%. For a mean leachate flow of 2.73 l s^{-1} and a calculated mean inlet waters input of 20.8 l s^{-1}, then for a loch water volume of 498486 m^3, mean residence time of water in the loch would be 245 days (8.06 months).

Although this percentage may be different in real terms from the actual ratio, due to a contribution from rainwater input and evaporation from the loch surface, the use of a tracer that forms an integral parameter in the system renders the treatment independent of such clean water inputs and outputs. It must however assume that the relative chemistry of the non-discrete water is similar to that of the north inlet. As the whole of the loch catchment lies on basalt bedrock or locally derived boulder clay this would appear to

be a reasonable assumption, although the relatively very high levels of sodium in the Whinnyhall Tip and Kirkton Burn spring waters must temper this assumption somewhat. It will also be affected by chemical inputs from the atmosphere; the only important one of which would be carbon dioxide. The uptake of carbon dioxide is very slow but with a water body as alkaline as Kinghorn Loch this may be expected to be significant. Despite a residence time of eight months the loch water did not assume any significant degree of equilibrium with atmospheric carbon dioxide and indeed, at the concentrations of hydroxide and carbonate found, the speciation model for the inorganic chemistry of the loch (see Chapter 6) predicted that the system was best described as completely closed with reference to carbon dioxide rather than open and therefore in atmospheric equilibrium. It will be seen in Chapter 4.7.4 that this assertion requires modification, but that from an inorganic equilibrium viewpoint, it generally holds true.

4.6. DETERMINATION OF GROSS MATERIAL LOSS TO THE SEDIMENT.

Table 4.4. summarises the mean values for relevant determinands for the north inlet water and leachate over the period January 1981 to May 1983 (as given in Appendix A) and uses the flows calculated above to determine the immediate concentrations that would be found in the mixed water.

These values are compared with the actual data for the loch water taken from the outlet in order to assertain what losses occured within the loch body. Listed with the mean is the standard deviation on the mean at 95% confidence limit. This has been calculated

DETERMINAND (dissolved)	NORTH INLET mean	s.d.	LEACHATE mean	s.d.	MIXTURE mean	s.d.	UNITS ($mg\ l^{-1}$)
calcium	43.4	1.083	4.031	0.339	38.8	0.968	
magnesium	22.4	0.581	0.988	0.186	19.9	0.506	
sodium	20.8	0.345	2006	48.40	250.4	5.008	
potassium	0.677	0.036	25.63	0.692	3.563	0.107	
aluminium	0.174	0.017	139.7	4.442	16.31	0.530	
alkalinity	139.4	3.506	4295	115.8	620	15.81	as $CaCO_3$
chloride	25.6	0.407	67.84	1.252	30.48	0.488	
sulphate	23.4	0.908	152.0	4.689	38.27	1.244	as S
silica	4.52	0.119	7.07	0.261	4.815	0.126	as Si
borate	0.06	0.003	0.823	0.054	0.148	0.008	as B
nitrate	7.19	0.163	1.839	0.121	6.57	0.149	as N
nitrite	0.018	0.002	0.366	0.038	0.059	0.006	as N
ammonia	0.147	0.024	0.681	0.035	0.209	0.031	as N
flouride	0.136	0.007	3.16	0.275	0.486	0.041	
orthophosphate	0.038	0.007	2.951	0.152	0.375	0.024	as P
arsenic	-----	-----	3.565	0.240	0.412	0.028	
vanadium	-----	-----	5.269	0.391	0.609	0.045	

TABLE 4.4. Calculated Mean Composition of Loch Water Prior to Deposition and Other Real Processes.

assuming the data for inlet and leachate respectively for each determinand are part of the same statistical set - a situation that is unlikely to strictly hold true when results are of a different order. However given the other uncertainties, primarily that of flow ratio and the uncertain chemistry of non-discrete waters, this assumption is reasonable.

Having compiled this estimate of initial chemical composition, it is possible to generate an estimate of gross loss within the loch by comparison with the real situation at the outlet. The loss of suspended solids exiting the loch was not significant (except for organic carbon) and can, in this consideration, be ignored. Table 4.5. calculates the gross loss for each determinand and places a degree of significance (at 95% c.l.) against each loss.

DETERMINAND (dissolved)	LOCH OUTLET mean	s.d.	LOSS mean	s.d.	SIGNIFICANCE	UNITS (mgl^{-1})
calcium	3.40	0.243	35.4	0.998	***	
magnesium	4.35	0.383	15.5	0.635	***	
sodium	249.6	3.675	0.8	6.211	---	
potassium	3.607	0.063	-0.044	0.124	n.s.	
aluminium	6.61	0.220	9.70	0.574	***	
alkalinity	470.1	8.25	150	17.83	***	as $CaCO_3$
chloride	37.84	0.566	-7.36	0.747	***	
sulphate	45.32	1.826	-7.05	2.209	**	as S
silica	1.199	0.041	3.616	0.133	***	as Si
borate	0.127	0.012	0.021	0.012	*	as B
nitrate	1.84	0.174	4.73	0.229	***	as N
nitrite	0.148	0.015	-0.089	0.016	***	as N
ammonia	0.264	0.026	-0.055	0.040	n.s.	as N
fluoride	1.476	0.064	-0.99	0.076	***	
orthophosphate	0.131	0.021	0.244	0.032	***	as P
arsenic	0.321	0.011	0.091	0.030	***	
vanadium	0.494	0.026	0.115	0.052	**	

TABLE 4.5. Estimation of Gross Loss of Material Within Kinghorn Loch, Indicating the Statistical Significance of any Loss.
n.s. not significant * significant at 90% c.l.
** significant at 95% c.l. *** significant at 99% or better

The calculation of losses, involving the difference between two uncertain estimates, contains an even larger degree of uncertainty and therefore a larger standard deviation. Note that loss of alkalinity includes non-carbonate alkalinity such as aluminate and silicate which would account for 79.8 mg l^{-1} expressed as $CaCO_3$. The adjusted carbonate-hydroxide alkalinity would therefore represent a loss of 70.2±13.7 mg l^{-1}. A few of the calculated mean losses are negative, indicating the gaining of material, which is evidently not possible. The gain in potassium is not significant and those of nitrite (significant at 95% c.l.) and ammonia (not significant) are related to the change in the status of nitrate. The gain in concentration of chloride ion is significant at 99.9% c.l. This high level of significance is produced because the level in both inlet and leachate varies very little and both concentrations are of the same

order. There is no apparent relationship between chloride content and road salting in the wintertime as no seasonal variation is evident. The increase is relatively insignificant at 7 mg l^{-1} and it was thought likely to have arisen from the ingress of sea water spray as the loch is situated only about 1 km from the Firth of Forth on the east side right around to the south-west and tends to be very exposed to the prevailing south-west wind. This gain would be 3800 mg m^{-2} $month^{-1}$ and represent a level of chloride in rain water of 61 mg l^{-1} or a mean fall of sea spray of 2.5 mm $year^{-1}$. During the period of study a rain gauge was set up at the golf course south of the Kirkton Burn but its operation was never satisfactory. However, water taken from this gauge contained a mean of 16 mg l^{-1} chloride and 4.7 mg l^{-1} sulphate (as S). Whereas this contribution to the chloride is inadequate to reduce its statistical significance it reduces the error to a gain of 5.4 mg l^{-1}. Because of the high level of sodium found in the loch the concomitant increase in sodium is insignificant.

The gain in sulphate is significant at 95% c.l. even allowing for the small contribution from rain water. A careful study of Table A.4. of the Appendix will show that west inlet water (when not showing signs of leachate ingress) contains 80-120 mg l^{-1} of sulphate compared to a north inlet mean of 23 mg l^{-1}. Thus if the estimated 32% of inlet water that is of non-discrete origin contained even a modestly increased level of sulphate then this gain would be explained and sulphur would be available for mineral and organic deposition. The gain in fluoride, though small, cannot be satisfactorily explained. It is significant at 99.9% c.l. The most likely cause of this is the

under-estimation of the fluoride content of the leachate, but a long-term mean of 10.8 mg l^{-1} would be required compared to a reported level of 3.16 mg l^{-1}. The reported values contain a large number of samples with very low fluoride contents (less than 0.5 mg l^{-1}) as well as high ones up to 19.5 mg l^{-1}. The selective ion technique has been found to be very reliable for a normal range of river waters and TISAB (total ionic strength adjustment buffer) gives efficient pH and complexation control. Recently however, Nicholson[20], in reviewing errors associated with this determination in digests of rock samples found that a minimum decomplexing time of 20 mins should be allowed and preferably that the buffer should be added to the sample during the previous day. This was not done for the fluoride determinations carried out during this study. Further it is stated that higher concentrations of aluminium may reduce the effectiveness of the buffer and that sample pretreatment may be required. Although the leachate would not contain the ionic concentrations found in rock digests, concentrations of potentially interfering ions were greatly in excess of those normally found in samples subjected to this analysis. Thus considerable doubt is cast on the determination of fluoride in the leachate and it is quite likely to have been under-estimated. No estimate is possible for sodium, as this was used for the flow budget calculation, but any sodium taken into clays will, in any case, be indeterminably small. This is emphasized by the very low sodium content in sediment matrix material (Table D.1.) and in experimental sedimentation studies (Chapter 4.10.). Table 4.6. tabulates the projected losses (for a surface area of 112560 m^2).

Table 4.6 would indicate a loss of 4615 mmol m^{-2} $year^{-1}$ of carbonates to the sediments as a result of the precipitation of alkalinity

DETERMINAND	MEAN (mmol m^{-2} $year^{-1}$)	RANGE	MEAN (mg m^{-2} $year^{-1}$)	RANGE	
calcium	5818	315	232700	12600	
magnesium	4242	341	101800	8180	
aluminuium	2357	276	63640	7450	
silicon	847	59.1	23716	1655	
alkalinity	4615	900	55380	10800	as C *
nitrogen	2206	210	30884	2940	
phosphorus	51.7	13.3	1602	413	
arsenic	7.95	0.53	596	39.4	
vanadium	14.84	13.4	757	683	
boron	12.5	14.32	138	158	

TABLE 4.6. Projected Annual Losses to the Sediment.
The range is set about the mean and is at 95% c.l.
* alkalinity contribution from CO_3-OH system only.

chemically derived from aqueous inputs. It is thus probable that a surplus of calcium is available to undergo deposition as calcite by biogenic processes involving the phytoplankton population using carbon derived from the atmosphere. Wetzel[21] found that several lakes containing phytoplankton at chlorophyll-a levels of 3-10 ug l^{-1}, absorbed carbon dioxide from the atmosphere at a rate of 1-15 mg l^{-1} $month^{-1}$. In Kinghorn Loch this would represent approximately 12-180 g m^{-2} $year^{-1}$ of C input. It will be seen in Chapter 7 that the chlorophyll-a levels in the loch have generally been well in excess of the above figure. Thus in addition to the carbonate flux to the sediments a considerable organic flux may be anticipated. Any such contribution will have been almost entirely generated by phytoplankton, as macrophytes were almost totally absent, particularly in later years, and debris from tree leaf-shedding would be limited.

If phytoplankton, by initial consumption of carbon dioxide during photosynthesis, were providing a driving force for its absorption into the water body then the prediction of the speciation model

indicating approximation to a closed system with respect to carbon dioxide is not accurate (although it is approximated to for inorganic speciation only). However thermodynamic non-equilibrium with respect to carbon dioxide remains evident.

4.7. SIGNIFICANT CHEMICAL AND BIOCHEMICAL PROCESSES

4.7.1. CARBONATE MINERAL FORMATION

In the vast majority of temperate natural situations it is considered that carbonate sedimentation occurs through biogenic processes[22]. Algal and bacterial action is normally responsible for conveying bicarbonate and calcium ions into a suitable environment from which precipitation can occur. This intervention is unnecessary in Kinghorn Loch waters as abundant carbonate ion is readily available. That calcite can be chemically generated within the system will be shown in Chapter 4.7.1.1. It is probable that some calcite is biotically produced but it is likely that this process is not dominant as the residual levels of calcium, carbonate and pH are not correlated with biological activity in the loch.

Several workers have investigated the rate of calcite production but most have been concerned with the marine environment. Kazmierczak *et al*[23] approached the subject by studying the rate of crystallisation in both a closed system and under maintained conditions of supersaturation and pH. Calcite, precipitated onto abundant calcite seed crystals, was produced with a first order rate constant (normalised to specific area of calcite seed) independent of the level of supersaturation. This confirmed the absence of secondary nucleation or intermediate processes, involving a mechanism of direct growth on the seed crystals. The observed rate of growth was such

that under the conditions of Kinghorn Loch at pH 10, generation of calcite would be essentially complete within 2 hours. Plummer et al[24] reported a rate of crystal growth (R), applicable to low pCO_2 values and near-neutral pH, such that

$$R = k(C_t - C_s)^2$$

where C_t is concentration of calcium at time t and C_s is the concentration at saturation and k is a growth constant. This relationship finds that growth is second order under these conditions.

Calcite crystal growth in the loch is likely to be affected by various interfering substances. Stewart and Wetzel[25] found that low levels of fulvic acid (<2 mg l^{-1}) were potent inhibitors of crystal growth. They considered that many such substances retard calcite formation by blocking spiral dislocation growth sites, forcing crystal growth by the much slower process of surface nucleation. Section 4.7.1.1 shows that the deposit formed from filtered leachate and inlet water was white and essentially devoid of organic carbon. It was apparent during this experiment that appreciable precipitation of deposit occured immediately even without available seed, and the rate of reaction will be further examined in Chapter 4.10.

The $\log([Ca^{++}]/[Mg^{++}])$ ratio in the loch prior to deposition approximated to 0.2. According to Figure 5.13 of Stumm and Morgan[8] this places the loch water just inside the area of stability for calcite rather than dolomite. It would not however preclude a mixed phase of calcite with some magnesium lattice positions. However dolomite should be the stable phase in seawater but no convincing evidence for its recent formation in seawater has been found[8]. Dolomite formation

(under saline conditions) is known to be extremely slow[26], whereas calcite formation is rapid. It is thought[8] that the formation of magnesium calcite may be kinetically more favourable. The experimentation in Chapter 4.7.1.1 produces a deposit with a small amount of magnesium incorporation (Mg/Ca <0.015) but this amount would be readily accounted for by the formation of aluminosilicates. XRD studies (Chapter 4.7.1.1) show no deviation from calcite structure.

4.7.1.1. EXPERIMENTAL PRECIPITATION STUDIES.

This experiment was conducted during 1984, after the diversion of the leachate. The leachate used was a "combined leachate" sampled from the outlet of the mixing pit at the exit of the pumped line going ultimately to the Kirkton Burn. This leachate comprised that which had been diverted from the loch plus that which historically drained to the Kirkton Burn. Table 4.7 tabulates the analysis of this leachate relative to the three-year mean for the leachate going to Kinghorn Loch.

determinand	"combined leachate"	leachate to loch	units
pH	12.6	12.1	
dis. Ca	7.5	4.0	mg/l
Mg	5.5	1.0	mg/l
Na	3585	2006	mg/l
K	57.3	25.6	mg/l
Al	137	140	mg/l
Fe	0.12	0.13	mg/l
V	2.8	5.3	mg/l
As	1.6	3.6	mg/l
SiO_2	63	7.0	mg/l Si
Cl	120	68	mg/l
alkalinity	7825	4295	mg/l $CaCO_3$
SO_4	166	154	mg/l S
PO_4	8.5	3.0	mg/l P
F	15	3.2	mg/l
NO_3	1.5	1.8	mg/l N
NH_3	3.0	0.7	mg/l N
B	0.99	0.82	mg/l

TABLE 4.7. Comparative analysis of "combined leachate".

20 l of inlet water was pressure filtered through a washed glass fibre disc (grade C) while 2 l of combined leachate was passed through a 0.45 um polycarbonate membrane. Two 10 l polythene bottles were thoroughly cleaned and 10 l of inlet water placed in each. The inlet water was stirred with a PTFE coated magnetic follower and leachate added dropwise at a rate of approximately 5 cm^3 min^{-1} until each batch was raised to a 1:50 and a 1:200 leachate:water ratio respectively. The addition of leachate was extremely slow in order to avoid any local concentration effects as suggested by Hayden and Rubin[27]. The followers were removed and rinsed into the mixture with distilled water. The bottles were capped and thoroughly agitated for 10 min. The bottled were retained in darkness at 20°C for 6 months and were thoroughly agitated for 10 min each day.

On removal the bottles were thoroughly shaken for 10 min and returned to the incubator overnight. The mixture was carefully syphoned from each bottle to half the original volume. The bottles were thoroughly shaken and settled overnight. A syphon was clamped into place in each bottle and the volume very slowly (approximately 50 cm^3 min^{-1}) reduced to 400 cm^3. No obvious sediment loss was observed. Each bottle was thoroughly shaken and the suspension thansferred to a very clean 500 cm^3 stoppered measuring cylinder. 2x50 cm^3 washings were added, using filtered water, and the cylinders settled overnight. The supernatent was drawn down to 50 cm^3 and each suspension transferred (with 2x5 cm^3 washings) to a centrifuge tube and sealed. Each suspension was centrifuged for 30 min and the liquid carefully removed with a Pasteur pipette. The residue was washed with 2x40 cm^3

water, each time centrifuging for 30 min. Finally 2 cm^3 water was added and the residues transferred to 50 cm^3 round bottomed flasks and frozen by swirling in liquid nitrogen. The residues were then freeze-dried. Table 4.8 illustrates the pH change occuring and the yield after 6 months.

sample ratio	immediate pH	immediate alkalinity	after 6 months pH	after 6 months alkalinity	yeild (mg)
1: 50	10.03	270	9.26	145	804
1:200	9.33	160	8.24	125	97.2

TABLE 4.8. Experimentally precipitated "natural" material.

The recovery of solid was calculated to be 75% for 1:50 and 28% for 1:200. Thus, a considerable risk exists that the solid recovered, particularly at a 1:200 ratio, will not be representative of the bulk of the deposit. It should, however, be representative of carbonate mineral formation. The original mixed solutions were both brown in colour but the deposits formed were white/pale cream. The freeze-dried deposits were ground in an agate mortar and pestle for 10 mins. Inorganic components were estimated using the thin-film procedure of Chapter 9.2.1.3 using 4 replicates of each analysed against 4 replicate blanks. A further 4 replicates were steeped in 5% acetic acid for 20 days before being removed, washed thoroughly with filtered distilled water and dried at 30°C overnight (see Chapter 9.2.1.3). Four replicates blanks were similarly treated. Aliquots were analysed for organic components as in Chapter 9.3, and further material was subjected to X-ray diffraction studies. Table 4.9 tabulates the results found. Results for elements determined by XRF have been normalized to a Ca:inorganic C ratio consistent with Ca existing as $CaCO_3$. Normalization is required due to inevitable

losses of material to the sides of glassware (N.B.Price, personal communication). Statistical appraisal of the absolute mass of sample on each replicate membrane (approximately 100 ug) indicates that mass per membrane is repoducible to the limits of detection shown below.

element	ratio 1: 50	1: 50(acid)	1:200	1:200(acid)
Si	1.8	<1	2.3	1.1
Al	<2	<2	<2	<2
Fe	<2	<2	<2	<2
Mg	0.6	<0.5	<0.5	<0.5
Ca	38.4	<0.5	38.8	1.03
K	<0.5	<0.5	<0.5	<0.5
P	<0.5	<0.5	<0.5	<0.5
Mn	<0.5	<0.5	<0.5	<0.5
Ti	<2	<2	<2	<2
inorganic C	11.15	----	11.64	----
organic C	<0.5	----	0.5	----

TABLE 4.9. Elemental analysis (%)of precipitated "natural" material. (acid) indicates pre-treatment with 5% acetic acid.

The results indicated that the deposits consisted almost entirely of calcium carbonate with up to 5% aluminosilicate production. Acid treatment removed virtually all of the calcium and approximately half of the silicon present indicating that most of the clay minerals formed were probably in a unstable and hydrated state.

4.7.2. CLAY MINERAL FORMATION.

Major elements normally considered to be associated with aluminosilicate production are Si, Al, Mg, Na, K, and Fe. Dissolved iron was not found in the loch water while any loss of sodium or potassium was very small and, in the case of sodium, which was present at such a high concentration, indeterminable. Si, Al, and Mg were lost to the sediment in the molal proportion 1:2.8:5, a ratio very deficient in silicon relative to most clay structures. The material formed may have been sedimented by aggregation or else by sorption onto iron

solids, calcite, or organic material. A hypothesis concerning the stoichiometry of these clay minerals is proposed in Chapter 5.7.3.

4.7.3. REMOVAL OF IRON TO THE SEDIMENT.

Iron is considered to have entered the loch almost entirely as red mud solids. The iron would exist as finely divided particulate hematite (Chapter 2.2.3), probably associated with clay minerals [28]. Iron was more or less evenly distributed throughout the surface sediments of the loch indicating a very fine particle size. At station 39 a heavier component is also evident. There is, however, no sign of particulate iron being washed from the loch. Wetzel[21] reported that phytoplankton accumulate iron to their needs. Some information given indicates a level in plankton of 950 ug g^{-1}. On this basis such an accumulation would account for only 3% of the iron input to the loch. Tipping et al[29] found that colloidal iron particles in Esthwaite Water in Cumbria consisted of 30-40% Fe and 30% organic material, of which one third was humic matter. Tipping and Ohnstad[30] concluded that surface properties were dominated by the humic components and this fundamental alteration of the iron oxyhydroxide surfaces has been noted by several workers concerned with trace metal sorption (e.g. Laxen[31]). Tipping and Ohnstad[30] found that even at near-neutral pH, free-cation (e.g.Ca^{++}) concentrations well in excess of those found in the loch were necessary to induce rapid flocculation. Also Tipping[32] found that adsorption of humic materials was greatly reduced at pH 8-10 relative to lower pH values. At the high pH of Kinghorn Loch, it was therefore unlikely that an unaided settlement would occur by this process.

The humic input to the loch was greatly exceeded by the autochthonous

(produced within the loch) input due to the high level of organic productivity. This material will not contain as high a carboxylate or phenate ion concentration as humic material and therefore will have less ability to coat iron solids[32]. Leppard[33] has tentatively correlated deposition of solids with polysaccharide, formed from fresh organic material, under certain conditions. The range of attractive surfaces was not identified but he found that polyvalent cations caused coagulation of the aggregates to macroscopic size. However, Sholkovitz and Copland[34] in a study of suspended matter in Lake Windermere, concluded that iron distribution was not affected by biological cycles within the lake. It is probable that, in Windermere, the abundance of humic materials will be sufficient to flocculate the limited supply of iron oxyhydroxide, and less efficient processes involving autochthonous organic materials will not be seen. Thus it is possible that in Kinghorn Loch sedimenting phytoplanktonic debris could be responsible for some aggregating of iron containing particles.

The other major input to the sediment was calcium carbonate. During the growth of calcite solid solutions may be formed with various metals, and several papers describe the existence of ferrous-calcites. The waters of Kinghorn Loch were predominantly oxic and there is little reason to believe that ferrous ions existed other than in the sediments or at the mud/water interface. Consequently sedimentation would involve only ferric oxyhydroxide. Clarke *et al*[35] and others, have recently studied the rapid precipitation of ferric ion on calcite by an acid/base reaction such that

$$2Fe^{3+} + 3CaCO_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3Ca^{3+} + 3CO_2$$

The rate of reaction was found to be related to the surface area of calcite. Thus during the formation of calcite in the loch the inclusion of iron oxyhydroxide into the structure may occur.

The remaining process that is possibly significant in the sedimentation of iron in the loch is that of ion exchange and flocculation of authigenic clay minerals. However flocculation will not be kinetically favoured, as iron oxyhydroxide will carry a substantial negative charge at pH 10 (Hohl et al[36]). The inclusion of the ferric ion in the lattice is unlikely. Tardy and Garrels[37] found that the production of various ferric silicate and aluminosilicate minerals was thermodynamically slightly favoured relative to goethite or hematite but that such a reaction was unknown.

4.7.4. SUPPLY AND DEPOSITION OF ORGANIC MATERIAL.

4.7.4.1. SOURCES OF ORGANIC CARBON.

Organic carbon is generally delivered to a lake in soluble form (Wetzel[21]). Most studies have found that detrital organic carbon greatly exceeds autochthonous material[21] and that dissolved carbon input is some ten times greater than particulate input. Chapter 2.2 concluded that the input of labile organic material via the leachate was negligible. The north inlet provided a maximum of 2.5 g m^{-2} yr^{-1} of labile organic carbon [based on a biochemical oxygen demand (B.O.D.) of 1 mg l^{-1} O]. This is probably an over-estimate as the B.O.D. of this water has rarely been >1 mg l^{-1} and has only come close to 1 mg l^{-1} at times when a polluted flow was seen to be issuing from the septic tank of the farm. It should be noted that the farm buildings were not used for agricultural purposes but as a

residential property. The septic tank effluent would consist of material almost fully represented by the measured B.O.D.

Another source of B.O.D. could be leaf leachate from fungal colonization of leaf packs in the water as this is known to constitute a significant input of organic carbon and nitrogen[38]. However in Kinghorn Loch, the north inlet travels underground from the reservoir and while above ground falls rapidly over stones and within shallow, grassy banks. Water cress occured over a 10 m length of the stream during summer and this will have produced some input, but other leaf autolysis inputs must be considered insignificant.

Consideration of back records of the F.R.P.B. indicates that the chemical oxygen demand (C.O.D.; see Chapter 9) of north inlet water was consistently <5 mg l^{-1} O. From experience with more humic waters in the area it is possible to estimate that the C.O.D. of this sparkingly clear water would, in fact, be well below this figure. Thus it is considered that the refractory input via the north inlet would be low (10 g m^{-2} yr^{-1} C for a C.O.D. of 4 mg l^{-1} O) but could represent a significant proportion of the refractory organic carbon found in the sediments. It is apparent that any percolate from the fields is also likely to contain a higher proportion of refractory humic material but groundwater inputs are generally found to be low in labile material[21].

Autochthonous material is supplied by photosynthesis, possibly from the littoral zone as well as from phytoplankton. Dissolved organic material is generated as extracellular excretions during growth phases and by autolysis during sedimentation[21]. Organic carbon

levels below phytoplankton activity is low under aerobic conditions, since the organic substances generated, including carbohydrates, proteinaceous compounds, and fatty acids are readily degraded by microorganisms and only polymeric aromatics (the end product of microbial degradation) and larger particles tend to be little degraded. This primary metabolism is supplemented by a vigorous secondary metabolism at the mud-water interface brought about by aerobic bacterial populations several orders of magnitude greater than in the water body. This secondary digestion is generally aided by faunal consumption. Dissolved organic material arrives at the interface by aggregation and co-precipitation with inorganic substances. Littoral flora provides more refractory, lignified tissue which is only slowly degraded.

In Kinghorn Loch the supply of organic material from littoral flora has steadily decreased. In 1978 substantial macrofloral beds still occured in the bay in the north-east corner of the loch and to the north of the outlet. Shallow water flora also existed behind the line of dead trees at the north-west but this area was above the water line for much of the year (see Figure 4.3), being within 100-200 mm of maximum loch level. By 1981 macroflora had retreated to small patches which dried out in the summertime and no growth occured in the bays near Craigencalt Farm. By 1985 these areas had not been recolonised. Deeper water along the southern shore, which had evidently supported a good crop of Polygonum amphibium, contained considerable debris, all of which appeared mummified in a thick crust of mineral deposit. Thus it may be seen that during the 1970's refractory organic supply from littoral sources will have steadily decreased, ultimately to minor proportions. Conversely it is evident

that phytoplankton blooms became rampant at this time, generating much larger quantities (see Figure 4.10) of more readily degraded material. Considerable oxygen sags occured at times (see Figures 4.5 and 4.6), allowing larger proportions of organic carbon to occasionally reach the sediment. This irregular input will have been evenly redistributed by sediment turbation. Bioturbation and faunal consumption will have been negligible.

It will be seen in Chapter 4.7.4.2 that phytoplanktonic activity is estimated to have provided over 300 g m^{-2} yr^{-1} of total organic carbon production with some 90 g m^{-2} yr^{-1} of organic carbon (<u>in toto</u>) being buried. Thus for Kinghorn Loch it is apparent that the major input of organic carbon to the loch water (although possibly not of refractory material to the sediment) is supplied from photosynthesis.

4.7.4.2. THE ROLE OF PHYTOPLANKTON.

Phytoplankton populations in Kinghorn Loch consisted almost entirely of <u>Oscillatoria</u>, a filamentous cyanobacteria ("blue-green algae") with an absence of significant zooplankton or diatoms (see Chapter 7). The production of "algal" protoplasm by photosynthesis and its subsequent heterotrophic respiration may be summarised by the reaction[8]:

$$106CO_2 + 16NO_3^- + HPO_4^{2-} + 122H_2O + 18H^+ + \text{trace elements} + \text{energy} \leftrightarrows [(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)] + 18O_2$$

"algal" protoplasm

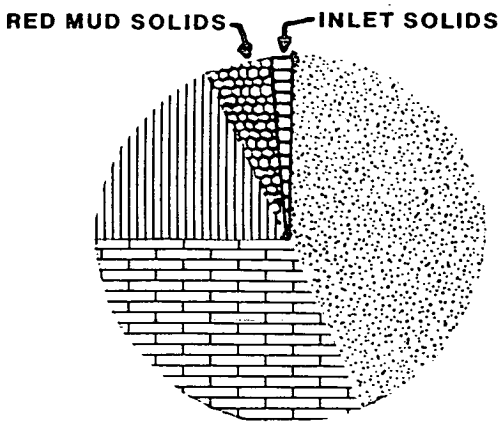
Cyanobacteria typically contain 46-49% C, 8-11% N and 0.7-1.1% P (Reynolds[39]).

The development and collapse of such blooms were very significant events and led to significant levels of C, N, S, and P in the sediment. Silica would not be lost by this process as cyanobacteria typically contain <0.1% Si dry weight.

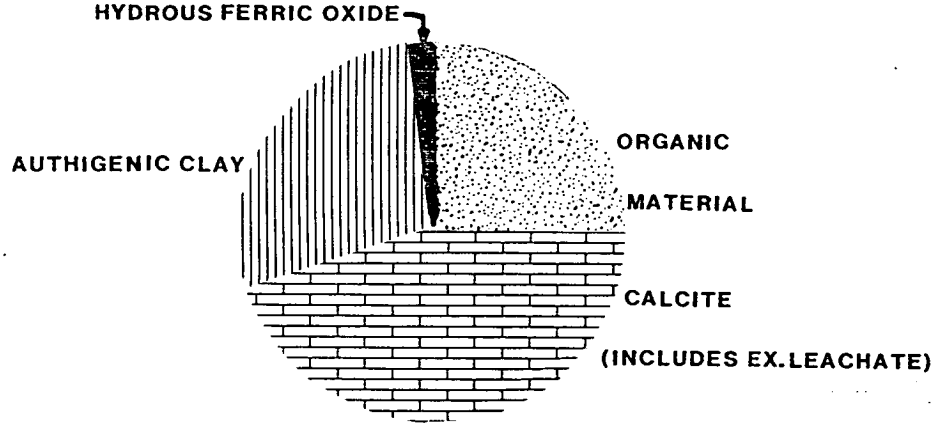
The three year mean for the levels of nitrogen and phosphorus in the loch indicate a loss of 4.8 mg l^{-1} and 0.24 mg l^{-1} respectively to the sediment or atmosphere. Initial assimilation of these elements will be to the phytoplankton. It should be noted that as well as soluble nitrate, cyanobacteria are able to fix dissolved nitrogen gas although this contribution is unlikely to have been significant[39]. As the material is degraded on passage to the sediment it becomes enriched with carbon relative to nitrogen and phosphorus. Released phosphorus will be partly sorbed by precipitating calcium carbonate or iron oxyhydroxide (Chapter 4.7.5), but nitrogen and most of the carbon would be recirculated. If it is assumed that carbon and nitrogen were recirculated in stoichiometric proportion then the mean standing Oscillatoria crop would have attained a concentration of 76 mg l^{-1} (given the formula for protoplasm above), taken throughout the volume of the loch. The mean observed chlorophyll-a was 70 ug l^{-1}, representing 0.09% of the "algal" mass. Individual results are set out in Figure 7.5, from which it will be evident that extremely wide confidence limits should be applied. Reynolds[39] reports a chlorophyll-a level of 0.84% for Oscillatoria agardhii although this is high relative to that found by Bailey-Watts[40] who, for Loch Leven, Kinross-shire, found 0.15-0.3% on a body weight basis. Bailey-Watts[41] also found that for a stressed, mixed population, especially following closely on the collapse of a dense bloom, that the percentage of chlorophyll-a in the seston (total suspended load of the lake)

could drop below 0.1%. The seston of Loch Leven comprised mainly phytoplanktonic material. Thus despite the need to make broad assumptions in calculating biomass and the inadequate control over the determination of chlorophyll-a (see Chapter 9) a standing mass of something like 80 mg l^{-1} (taken as if over the full volume) as a three year mean does not seem unreasonable. This represents approximately 300 g m^{-2} yr^{-1} as CH_2O to the sediment, if it is assumed that solids leaving the loch normally consisted entirely of phytoplanktonic remains. Refractory inorganic material made up approximately 12% of the exiting solids (Table A.5). The excess of production over recyling within the loch would appear to have been something like 500 g m^{-2} yr^{-1}. This compares with a gross standing production figure for a temperate, eutrophic lake, as quoted by Wetzel[21], of approximately 900 g m^{-2} yr^{-1}.

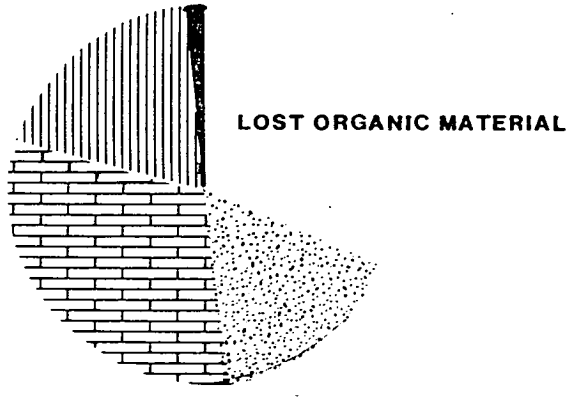
Using information provided by Wetzel and including other material generated within, and flowing to the loch, a gross estimate of sedimenting flux may be represented as in Figure 4.7(a). The measured concentrations in the top 30 mm of core '14' are represented in 4.7(b) while Figure 4.7(c) represents these concentrations with carbonate formation normalised to the supply indicated in (a). This indicates that, after allowing for the undifferentiated 'red mud solids' contribution in (a), some 60% of the precipitating organic material could be decomposed completely prior to reaching the mud/water interface or soon afterwards. This level of loss is to be expected for an oxic lake[21,34] and is evidenced by the dissolved oxygen profiles in Figures 4.5 and 4.6. Although these figures are based on a literature estimate, it is unlikely that a lake, so obviously suffering from substantial and long-lasting blooms, would



(a) material going to the sediment.



(b) composition of top of core 14.



(c) composition of sediment normalised to calcite content.

FIGURE 4.7. Supply and loss of material to the sediment.

have an organic carbon precipitation rate any lower than this mean estimate. The 'excess' production figure calculated above would therefore appear realistic.

Nitrogen input to the loch represented 7.1 mg l^{-1} N whereas the level in the loch body was 2.3 mg l^{-1} N. The difference represents 31.6 g m^{-2} yr^{-1} net loss to the sediment or 2.2% of sediment mass. This compares with measured values of 1.01-0.57% found in the upper part of core 14, and the significant difference must represent the level of denitrification occuring in the sediment and which will be considered in Chapter 5.7.4.

Phosphorus input to the loch stood at 0.37 mg l^{-1} for a three year mean, while the loch water contained 0.13 mg l^{-1}. The difference of 0.24 mg l^{-1} represents material lost to the sediment by mineral sorption and by inclusion in the sedimenting organic fraction. This represents 0.11% of the sediment which is not significantly different to the 0.2% P found in the recent sediment of core 14. The mechanism of co-precipitation will be considered in Chapter 4.7.5.

4.7.5. SEDIMENTATION CONTROL OF PHOSPHORUS.

Three significant routes exist for the removal of inorganic phosphorus from solution[21]:

(1) as apatite (usually co-precipitated with calcite)

(2) covalently bonded to hydrated iron oxides

(3) as organic phosphorus

(4) clay mineral adsorption (only significant at low pH)

Apatite [$Ca_{10}(PO_4)_6(OH)_2$] and stengite ($FePO_4.2H_2O$) tend to form under different environments. Whereas apatite is the usual sink in

marine environments iron phosphate tends to be more common in freshwater systems[8]. In areas such as eutrophic lakes substituted apatites such as francolite [$Ca_{10}(PO_4,CO_3)_nF_2$: where n<=6 for charge balance] may form but the main sink in many lakes normally consists of chemisorption onto hydrous iron oxides.

Apatite is increasingly stable relative to calcite as the pH increases and is further stabilised by the formation of mixed phases and of substituted apatites[8]. The formation of apatite is very slow[42] and inhibited by magnesium. Thus co-precipitation with growing calcite is more likely, particularly in a system like Kinghorn Loch with fine growth occuring apparently throughout the loch, with apatite forming a minor part of the structure. Murphy et al[43] found that, in the absence of calcite formation, little removal of soluble orthophosphate occured in eutrophic, calcitic lakes in British Columbia, while calcite formation completely removed orthophosphate. The removal of phosphorus was not correlated with primary production or biomass. Other workers such as Koschel et al[44] and Avnimelech[45] have arrived at similar conclusions, involving the formation of surface complexes such as $Ca_3(HCO_3)_3PO_4$.

However, such a mechanism probably depends on an absence of iron oxyhydroxide deposition. Wetzel[21] reported a lack of correlation between calcite and phosphorus in the sediment of a range of lakes and reported more complete removal in low calcium lakes with more substantial Fe(III) levels. Kinghorn Loch provides a sestonic supply of both fine grained calcite and hydrated iron oxides, so both processes are likely to occur. On balance however, since phosphorus is known to form very strong bonds with iron, it would appear that

chemisorption onto hematite is probably favoured for the removal of inorganic phosphorus.

The deposition rate for phytoplanktonic debris of approximately 300 g m^{-2} yr^{-1} may have been sufficient to account for most of the loss of phosphorus to the sediment. As organic material is degraded the C:P ratio increases greatly. No estimate is available as to the degree of degradation occuring prior to reaching the mud/water interface in Kinghorn Loch so no estimate of the phosphorus deposition by this means can be provided.

4.7.6. SORPTION OF ARSENIC.

Arsenic occured in the loch to the extent of 320 ug l^{-1} (three-year mean). It entered as soluble species, although that measured within the loch body may not have been. However, on occasions, both dissolved and total arsenic were determined and no significant difference was found. A nationwide survey[18] found that Kinghorn Loch contained the highest level of dissolved arsenic in the U.K., although several rivers in south-west England contained higher levels of total arsenic. During this survey a figure of 500 ug l^{-1} was recorded for both dissolved and total arsenic, with a general level countrywide of <5 ug l^{-1}. The report proposed an Environmental Quality Standard (EQS) of 50 ug l^{-1} for the protection of freshwater fish. In April 1985 a survey of the loch was carried out in order to determine its suitability for stocking with rainbow trout. Despite the evident recovery of the loch the water body at the outlet possessed a dissolved arsenic level only just within the EQS. It has been strongly argued by Faust et al[46] that sediment levels of arsenic provide the major transport and distribution control even under

conditions of high aqueous arsenic loadings, and Tables 5.18 and 5.19 certainly indicates this to be so, with arsenic levels in the interstitial water of the upper 30 mm of the sediment being at least 100 times greater than the north inlet water supply. It is also evident that levels deeper in the core are adequate to maintain this supply for some considerable time.

Table 4.10 indicates the species of arsenic commonly found in water.

species		abb'n	oxidation state	phase
$HAsO_4^{2-}$	arsenate		+5	aqueous
$HAsO_2^{o}$	arsenite		+3	aqueous
$CH_3AsO(OH)_2$	monomethylarsonic acid	MMAA	+3	aqueous
$(CH_3)_2AsOOH$	dimethylarsinic acid	DMAA	+1	aqueous
AsH_3	arsine		-3	gaseous
$(CH_3)_2AsH$	dimethylarsine		-3	gaseous
$(CH_3)_3As$	trimethylarsine		-3	gaseous

TABLE 4.10. Species of arsenic commonly found in water

Phytoplankton are known to accumulate arsenic to several thousand times concentration but fish and invertebrates apparently do not[18,47]. Fish are known to ingest trimethylarsine, generated by phytoplankton, directly but the arsenic is rapidly released (95% within a few days)[47]. During 1985, phytoplankton levels were very low and zooplankton were found to contain arsenic at 0.55 ug g^{-1} wet weight (8.5 ug g^{-1} dry weight), while chironomids (primarily Chironomus plumosus) contained 2.5 ug g^{-1} wet weight (dry weight concentration not available). These figures compared with reported

values of 21-38 and 4.4-53 $\mu g\ g^{-1}$ dry weight for zooplankton and chironomidae respectively in "clean" water[18]. Thus it is evident that arsenic was not being concentrated into these invertebrates.

Arsenic would be expected to occur as the arsenate ion ($HAsO_4^{2-}$) at pH 8-10 under oxic conditions. Using data for the reaction

$$HAsO_4^{2-} + 4H^+ + 2e \leftrightharpoons HAsO_2^o + 2H_2O$$

given by Lemmo et al[48] $HAsO_2^o$ would become dominant at Eh -31 mV for pH 8 and -260 mV for pH 10 at 12°C. However the As(V) = As(III) transformation is very slow and different reactions are brought about by micro-organisms. Faust et al[46] found that for an oxic lake, Union Lake in New Jersey, receiving arsenic loads of approximately 2.8 mg l^{-1} (96% of which was dissolved) monomethylarsonic acid was dominant with an order of prevalence of MMAA> As(III)> As(V)> DMAA. Only about 60-80% of the total arsenic present was accounted for by these species. These authors interpreted these results by considering that most of the arsenic supply had been assimilated by micro-organisms where the reaction

$$As^{5+} \longrightarrow As^{3+} \longrightarrow MMAA \longrightarrow DMAA \longrightarrow As(H,CH_3)_3$$

is known to occur under increasingly reductive microenvironments[49]. It has been found that phytoplankton readily reduce arsenic to trimethylarsine[47] which may then be lost to the atmosphere. On release of these lower oxidation state species from the organisms non-catalysed oxidation is very slow[48] so MMAA and arsenite tend to persist. The transformation may however be catalysed biotically and also by Mn^{4+} according to the reaction[48]

$$MnO_2 + HAsO_2 + 2H^+ \leftrightharpoons Mn^{2+} + H_3AsO_4$$

Fe^{3+} may perform a similar catalytic function but the reaction is considerably slower. Arsenate and arsenite are generally considered to be of more or less equal toxicity to fish and mammals, while invertebrates are considerably more tolerant[18]. Organic species are generally less toxic and when combined into body tissue have very low toxicity[47].

The determination of the speciation of arsenic is an involved and time-consuming procedure and could not be attempted within the time-table for the study. The speciation is however important for the determination of mechanisms for removal of the metal to the sediment, As^{5+} being more readily removed than other species. Arsenic competes with phosphorus during deposition and is strongly sorbed onto hydrous iron oxides. However phosphorus is more effectively scavenged[50]. This process is considered to be by covalent bonding of the sort $-Fe-O-AsO(OH)_2$ rather than adsorption[51] and is of decreasing effectiveness as the pH increases[48] due to the increasing negative charge on the iron oxyhydroxide surface.

Arsenic is effectively adsorbed by clay surfaces and may form direct bonds through -SH and $-NH_2$ groups on organic matter[51]. Sorption of arsenic is greatly enhanced by finer particle size of absorbants.

Under the high pH conditions found in Kinghorn Loch As^{5+} may also be directly precipitated as $FeAsO_4$ or $Pb_3(AsO_4)_2$ whose solubility products may be exceeded[48]. However the rate of formation of these species is known to be extremely slow[52]. Thus, the most likely route for its removal must be by way of debris of the phytoplankton in which it may have become greatly concentrated[48,18]. Loss is also likely to occur to the atmosphere, as methylated arsines.

Lueschow[53] investigated the effect of the long-term (1926-1964) application of sodium arsenite (for weed control) on public lakes in Pewaukee, Wisconsin. He found levels which reached 460 ug l^{-1} and which were consistently above 100 ug l^{-1}. Fisheries were not apparently affected by the treatment. A specimen of Cladocera sp contained 1258 mg kg^{-1} As dry weight, but invertebrates did not concentrate arsenic. Surficial lake muds developed a mean level of 200 mg kg^{-1} with invertebrates able to tolerate up to 1920 mg kg^{-1} in the mud. The accumulation of arsenic in muds and water column ties in well with that found in Kinghorn Loch (Chapter 5.7.6.) Invertebrate populations were of similar species to those found in Kinghorn Loch and will be considered in Chapter 7.

4.7.7. FATE OF VANADIUM.

Vanadium was present in the loch to a mean concentration of 494 ug l^{-1} at the outlet. Data for the level of vanadium commonly found in natural freshwaters in the U.K., Europe and North America are very sparse but according to Orvini et al[54], 0.1-1.5 ug l^{-1} are typical values for lakes. 2 ug l^{-1} indicates pollution with levels up to 50 ug l^{-1} being exceptional and occuring in only a few special circumstances. Thus the vanadium levels found in the loch were quite exceptional. These reported levels are for total vanadium, occuring in dissolved and suspended form, and originating from detrital minerals and atmospheric inputs. Data on dissolved levels found in waters are extremely limited. No Environmental Quality Standard (EQS) is currently available but is under consideration. Indications are that a level of 100 ug l^{-1} would be adequate to protect a fishery in a water of moderate hardness such as found in the recovered state of Kinghorn Loch.

Laboratory studies and thermodynamic considerations indicate that V^{5+} is stable under full oxygen saturation while V^{4+} should be preferred under reducing conditions. Orvini et al[54], in considering the species present in natural waters was unable to draw a definitive conclusion, but did conclude that vanadium existed as inorganic monoions and not to any extent as organic complexes or polyions. Kinghorn Loch contained approximately 10^{-4} M vanadium and this is thought to be the threshold for the formation of polyanions of V^{5+}. It would probably occur in the loch primarily as vanadate, $VO_3(OH)^{2-}$, but polyanions of V^{4+} would also occur.

Two studies (Tong et al[55], Tong et al[56]) suggest that vanadium is not bioaccumulated by fish, with levels generally found to be <1 mg kg^{-1} with a maximum of 2.9 mg kg^{-1}. No data is available for bioaccumulation or toxicity to invertebrates. Marine phytoplankton appear to bioaccumulate vanadium to a moderate extent[57]. Vanadium is phytotoxic to crops at 10 mg kg^{-1} in sandy soils but since it is strongly sorbed by humic material[58] in soils and is known to sorb onto humic particles in water[54] such toxicity is likely to be greatly reduced in organic muds. I have been unable to locate any information concerning sorption by hydrous iron oxide, clays or calcite. However, the apparent dependence of toxicity on hardness, would suggest that an interaction with calcite can occur.

The input to the loch from the leachate represented approximately 600 ug l^{-1} in the water. Thus the indicated loss to the sediment was 0.73 g m^{-2} yr^{-1} or 490 mg kg^{-1} in the sediment. This loss is evidenced by the elevated levels of vanadium found in the muds and deposition will have occured by sorption onto phytoplankton debris or

assimilation by the growing bloom. Deposition by the inorganic suspended components is also probable.

4.8. SUMMARY OF PROCESSES CONTROLLING AQUATIC CHEMISTRY.

Figure 4.8 summarises in graphical form the inter-relationship between the processes described in Chapter 4.7 resulting in various depositions to the sediment. Estimates are given for a three year (1981-1983) period with concentrations in mg l^{-1} (of the primary element e.g. PO_4^{3-} as P) for determinands taking part in any particular reaction, and in square parentheses, [ ], for loadings in g m^{-2} yr^{-1}. The reliability of these data is very variable and will have been considered in the appropriate section. Note that although a certain amount of calcite is shown as biotically derived, it may well be the product of abiotic reaction involving biotically generated carbonate ion. Arrows indicate the net direction of reaction and many of these reactions will be finitely reversible. Recirculation of anaerobically generated products from the sediment is shown with dashed lines. Transformations occuring within the sediment and at the mud/water interface are considered in Chapter 5.

Collation of data from Chapter 4 allows an estimate of sedimentation to and within the loch to be compiled. Thus significant annual inputs to the loch may be summarised as follows:

Detrital: 5000 kg of suspended solids in north inlet water
8500 kg of aluminosilicate ex. red mud solids
6200 kg as Fe_2O_3 ex. red mud solids

Authigenic: 7000 kg suspended solids in leachate (80-85% as $CaCO_3$)

70000 kg carbonate mineral (as $CaCO_3$) formed in loch

40000 kg aluminosilicate mineral formed in loch

Organic: 26000 kg debris from phytoplankton production

1500 kg humic material derived from inlets

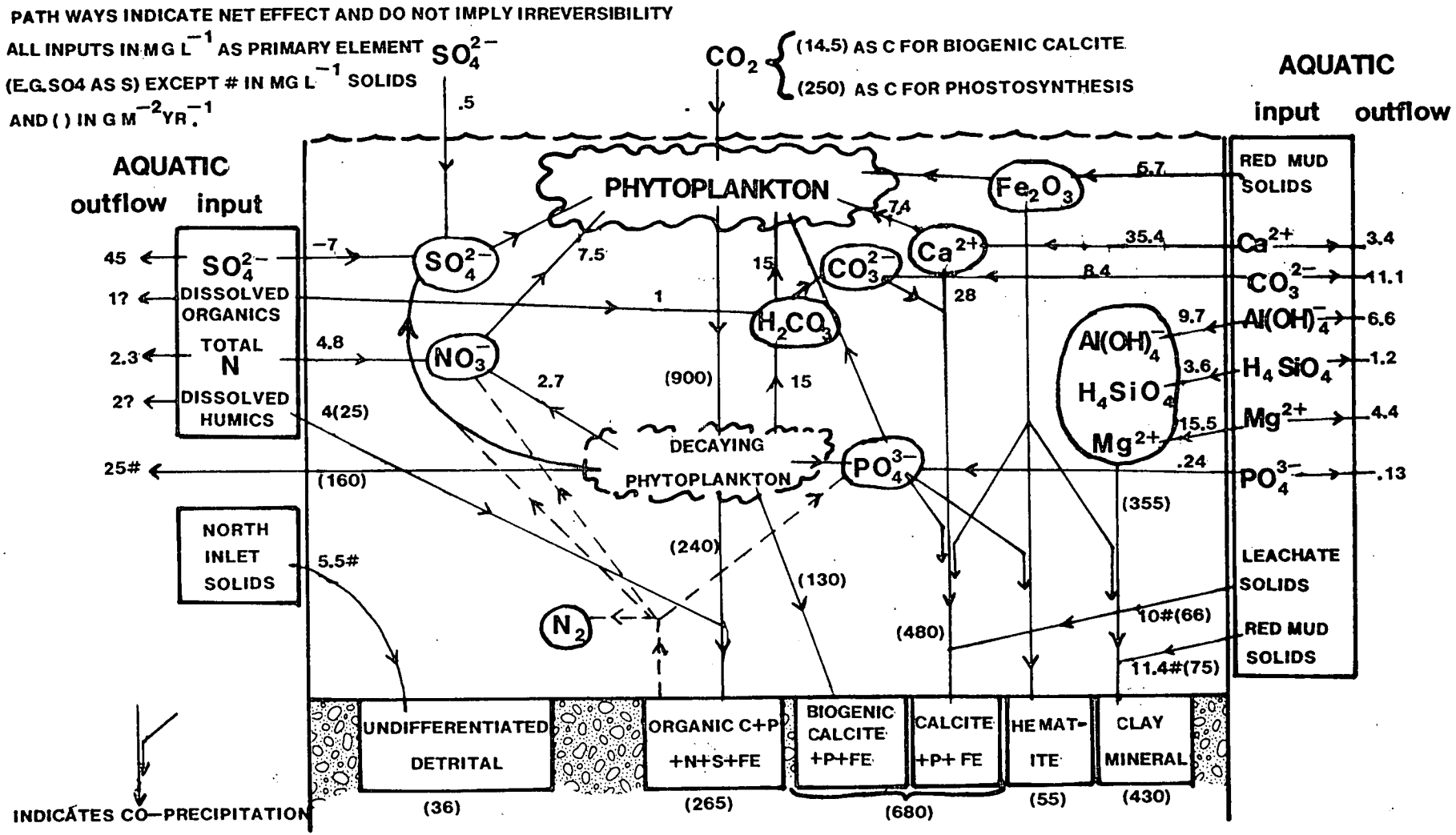
This represents approximately 1.5 kg m^{-2} yr^{-1} net deposition to the sediment.

4.9. PREDICTED LOSSES TO THE SEDIMENT 1950-1983.

No information is available to assist in quantifying the input to sediment prior to 1981, except for long-term pH measurement, which unfortunately is rather sparse, and the observation that severe blooms began to appear in the loch "in the 1970's". The water chemistry of 1950 can be predicted from that of the 1985 post-recovery situation. It is probable that significant ingress of leachate began in the late-1950's with a considerable rise in pH in the early 1960's. The situation stabilised somewhat until 1978 when further deterioration occured. This was probably as much due to exhaustion of the native water's buffering capacity as to the increase in leachate supply. Figure 4.9 illustrates the probable trend in major element input to the loch water body.

Figure 4.10 illustrates the quantity and type of material being formed within the water column of the loch. It is likely that both carbonate and authigenic clay mineral formation will have levelled out somewhat by about 1980 with the exhaustion of available calcium, magnesium and silicon supply from native waters. However, this levelling off of deposition will be less pronounced for clay mineral formation due to the variety of minerals that may form. The organic

FIGURE 4.8. Depositional pathways for major elements.



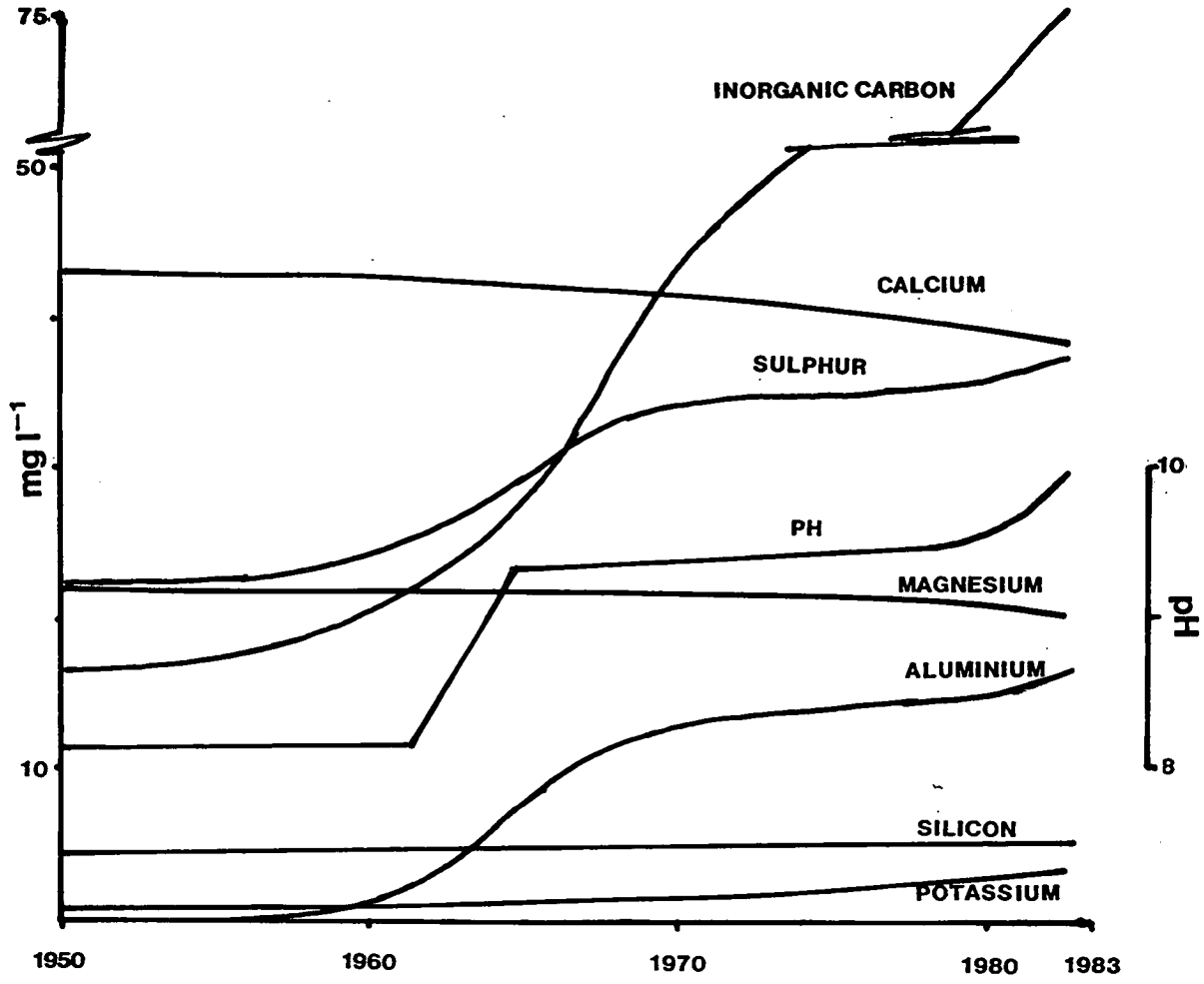


FIGURE 4.9. Elemental inputs to Kinghorn Loch.

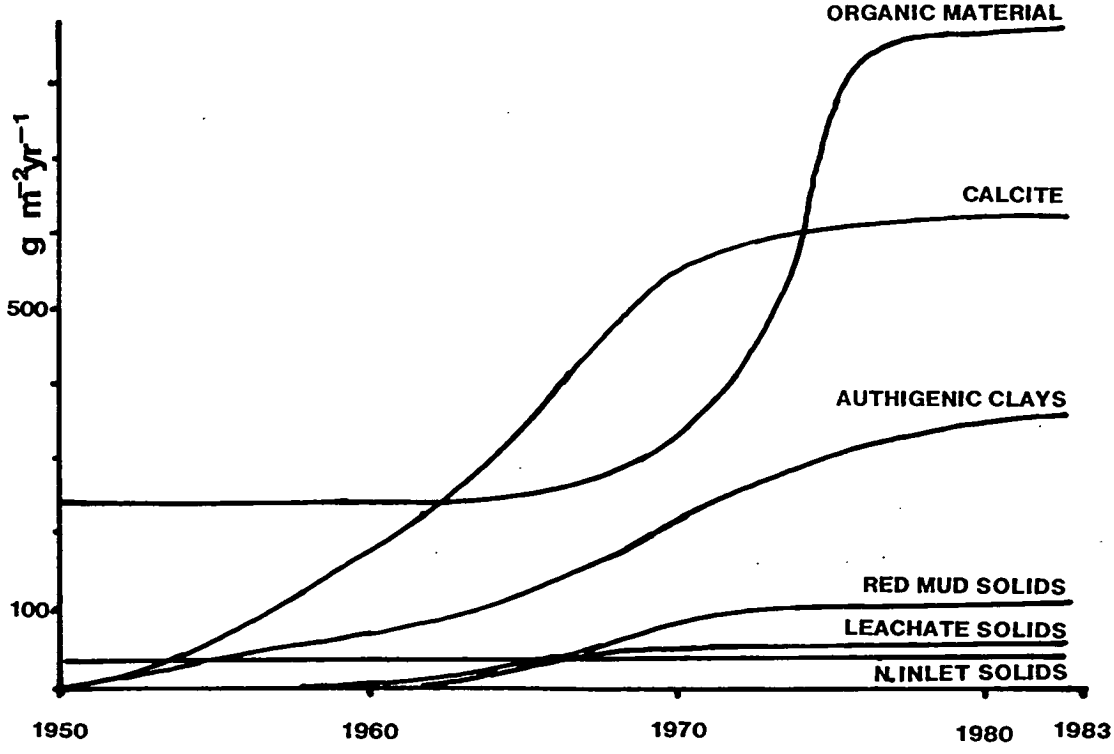


FIGURE 4.10. Sedimenting material in the water column.

material being generated in the loch was produced erratically and no meaningful mean figure for supply could be obtained. Taking information from Wetzel[21] for temporate lakes, the oligotrophic phase is likely to have received some 250 g m^{-2} yr^{-1} of organic material [as $(CH_2O)_n$] while the eutrophic phase, developed since the mid-1970's will have generated approximately 900 g m^{-2} yr^{-1} of material of which some 40% will have been incorporated into the sediment (see Chapter 4.7.4).

In addition to these major contributions, two atmospheric inputs are significant. Lead is found at a level of approximately 50 mg kg^{-1} in the sediments (Table D.1.) and, as considered in Chapter 2.2.1, must be of predominantly atmospheric origin. Zinc is an element that will be considered further in Chapter 5. Aqueous inputs to the loch (including suspended matter) contribute 1250 g yr^{-1} to the sediments which represents approximately 10 mg kg^{-1} in recent times. Atmospheric inputs for 1974[59] fell within the range 40-260 mg m^{-2} yr^{-1}. Atmospheric levels were found to be generally quite stable from 1950 to 1974. A mean 100 mg m^{-2} yr^{-1} deposition would represent a level of 82 mg kg^{-1} going to the sediment. The level in the sediments of core 14 was found to be approximately 80 mg kg^{-1} (Table D.1). Peirson et al[60] considered power generation stations as being major sources of atmospheric zinc. Large electrical generation plants occur to the south and west of Kinghorn and will provide a moderate contribution to these figures. It is not known what contribution red mud solids may have made since unfortunately trace metal data for red mud, analysed by an XRF technique, was lost on attempted retrieval, so this information is not available.

4.10. EXPERIMENTAL CHEMICAL PRECIPITATION STUDIES.

4.10.1. KINETICS OF PRECIPITATION.

The following section was set out to examine the rate of production of chemical precipitates in a simulated loch water situation in order to determine the order of reaction with respect to the major mineral forming elements. In order to cover the developing situation a range of flow ratios was used, and the experiments carried out at two temperatures in a carbon dioxide free atmosphere, to simulate a closed system.

APPARATUS.

For each dilution:

Polythene bottle (1 l) with unpigmented polypropylene, air-tight screw cap with holes for the tight fitting of two pieces of 1.3 mm (i.d.) P.V.C. tubing.

P.V.C. tubing, connected to cylinder of compressed air supply via 0.45 um sealed unit in-line membrane filter. Flow controlled by adjustable clip.

P.V.C. tubing exiting the bottle and passing into distilled water in a 500 cm^3 flask fitted with paraffin film cover.

Incubator set at 8°C

Incubator set at 25°C

METHODOLOGY.

Two bottles of 1 l of filtered leachate (sampled at exit to settlement pond) were equilibrated to 8°C and 25°C respectively. Three sample bottles, each containing 1 l filtered inlet water, were fitted with tubes as above and equilibrated to each of the required temperatures. A bottle was removed and the water stirred by means of a

magnetic stirrer so as to allow efficient mixing without gas entrainment. The required amount of leachate was added over a period of ten seconds. 100 cm^3 of solution was removed (and immediately filtered for suspended solids determination as described in Chapter 9) and the pH measured, at 30 s, 1 min and 5 min and the bottle returned to the incubator. 50 cm^3 of the filtrate from the suspended solids determination was placed in a 60 cm^3 polythene bottle and acidified with 0.5 cm^3 hydrochloric acid for metals and reactive silica analysis. Analyses were performed as described in Chapter 9. The procedure was repeated with the remaining five bottles. Each bottle was removed at time intervals of 15 min, 30 min, 1 hr, 3 hr, 20 hr, 90 hr, 180 hr and 500 hr and thoroughly shaken prior to sub-sampling and pH measurement. The reaction bottle was immediately returned to the incubator. The air above the solution in all the bottles was gassed at a rate of approximately 10 bubbles each minute for the whole of the experiment, and the incubator temperatures checked regularly. Control remained within ±0.5°C with 90% of results within 0.2°C. After 200 hours the bottles were temporarily placed in thermostated water baths to allow defrosting of the incubators. Suspended solids was determined as a guide only, since encrustation of the bottles with solids would remove solids from suspension.

EVALUATION OF KINETICS.

Table 4.11 tabulates the results obtained from these experiments. Kinetics were investigated by means of a linear fit to equations for order such that the rate constant (k) is calculated thus, for:

1st order time vs. $\log_{10}$(conc) gives a slope of $-k\ s^{-1}$

2nd order time vs. 1/(conc) gives a slope of $k\ mM^{-1}s^{-1}$

3rd order time vs. $1/(conc)^2$ gives a slope of $2k\ mM^{-2}s^{-1}$

To allow calculation of part order reactions the following procedure was described in Moore and Pearson[61] attributed to R.W.Wilkinson.

(1) Ratio of 1:5 leachate:inlet

time : determinand:	30s	1min	5min	15min	30min	1hr	3hr	20hr	90hr	180hr	500hr
pH	10.8	10.8	10.6	10.5	10.5	10.4	10.3	9.9	9.4	8.7	8.7
susp.solids	8	9	32	68	141	169	175	188	190	202	202
aluminium	15.9	15.8	12.2	10.8	9.4	8.5	8.3	7.2	6.3	5.0	1.9
calcium	7.1	7.6	7.8	8.5	1.7	0.5	0.1	<0.1	0.1	<0.1	0.2
silicon	5.2	5.4	4.3	4.0	3.6	3.5	3.1	2.1	1.0	0.6	0.5
magnesium	12.2	12.5	7.9	4.3	2.5	1.5	0.8	0.6	0.7	1.1	1.5

(2) Ratio of 1:10 leachate:inlet

time : determinand:	30s	1min	5min	15min	30min	1hr	3hr	20hr	90hr	180hr	500hr
pH	10.2	10.2	10.2	10.1	10.1	10.1	9.9	9.5	8.5	8.5	8.6
susp.solids	3	2	3	4	3	2	43	38	40	46	52
aluminium	9.8	10.7	10.0	9.7	8.7	8.2	-.-	8.2	5.9	2.8	1.4
calcium	12.6	12.2	12.9	12.9	12.9	12.1	2.5	1.1	1.8	3.1	4
silicon	5.1	5.0	5.2	5.2	5.0	5.0	5.0	4.5	2.8	1.4	0.7
magnesium	16.4	16.4	16.7	16.7	16.4	16.3	14.0	12.1	12.9	13.0	12.7

(3) Ratio of 1:50 leachate:inlet

time : determinand:	30s	1min	5min	15min	30min	1hr	3hr	20hr	90hr	180hr	500hr
pH	9.3	9.3	9.4	9.3	9.3	9.2	9.2	8.3	8.3	8.4	8.3
susp.solids	<1	<1	2	2	2	3	4	4	8	12	24
aluminium	2.2	2.2	2.3	2.1	2.0	2.0	2.0	1.7	0.7	0.5	0.2
calcium	21.2	20.9	21.2	21.3	21.3	21.4	20.7	19.3	17.2	16.0	13.0
silicon	4.8	4.7	4.8	4.7	4.7	4.8	4.7	4.1	3.1	2.8	2.7
magnesium	17.8	17.8	17.9	17.8	17.9	18.5	18.4	17.9	17.7	17.4	17.1

All results are in mg l^{-1}.

TABLE 4.11(a). Results of kinetics experiment for samples incubated at 8°C.

(1) Ratio of 1:5 leachate:inlet

time : determinand:	30s	1min	5min	15min	30min	1hr	3hr	20hr	90hr	180hr	500hr
pH	10.4	10.4	10.4	10.4	10.3	10.3	10.1	9.9	9.2	8.8	8.9
susp.solids	52	58	81	161	176	175	182	196	196	210	271
aluminium	11.8	10.4	9.9	9.4	9.5	9.9	9.9	8.6	7.8	5.7	2.4
calcium	8.6	8.6	8.4	0.7	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	0.1
silicon	4.9	4.7	4.5	4.4	4.2	4.1	3.9	3.3	2.0	1.3	1.1
magnesium	4.8	3.1	1.6	0.5	0.3	0.2	0.2	0.2	0.3	0.4	0.8
potassium	4.0	3.8	4.0	4.0	4.0	4.0	4.0	3.8	4.1	4.1	4.0

(2) Ratio of 1:10 leachate:inlet

time : determinand:	30s	1min	5min	15min	30min	1hr	3hr	20hr	90hr	180hr	500hr
pH	10.1	10.1	10.0	9.9	9.9	9.8	9.6	8.9	8.5	8.7	8.8
susp.solids	5	5	19	-.-	133	153	160	168	188	184	256
aluminium	8.7	8.6	7.7	5.8	4.9	4.0	3.4	2.3	2.0	1.7	1.9
calcium	12.5	13.1	12.2	2.5	1.1	0.6	0.5	0.5	0.6	0.7	1.1
silicon	5.1	5.1	4.7	4.1	3.7	3.4	2.4	2.0	1.6	1.5	1.5
magnesium	16.1	16.5	14.5	9.6	7.3	5.9	5.1	4.7	5.1	5.3	7.5

(3) Ratio of 1:50 leachate:inlet

time : determinand:	30s	1min	5min	15min	30min	1hr	3hr	20hr	90hr	180hr	500hr
pH	9.3	9.3	9.3	9.3	9.2	9.1	8.9	8.4	8.4	8.5	8.4
susp.solids	2	3	3	2	5	12	10	10	12	30	27
aluminium	1.8	1.8	2.0	1.8	2.0	1.8	1.9	1.8	1.9	1.5	1.5
calcium	20.4	21.0	21.6	20.9	20.9	17.0	10.9	8.2	7.8	7.9	5.8
silicon	4.6	4.7	4.9	4.8	4.8	4.8	4.8	4.5	4.7	4.5	4.9
magnesium	17.6	17.7	18.7	18.2	18.4	18.4	17.8	16.6	17.6	17.8	17.9

C. STARTER CONCENTRATIONS

ratio :leachate determinand:	1:5	1:10	1:50	inlet	
pH(*)	12.0	10.8	10.2	9.3	8.1	
alkalinity	3950				120	as $CaCO_3$
aluminium	115	19.3	10.5	2.4	0.1	
calcium	0.2	19.8	21.6	23.2	23.7	
silicon	9.2	11.8	11.1	10.4	4.8	
magnesium	0.1	15.9	17.3	18.6	19.0	
potassium	20.2	3.7			0.4	

All results are in mg l^{-1}.
(*) initial pH of mixtures calculated by speciation model.

TABLE 4.11(b). Results of kinetics experiment for samples incubated at 25°C.

Integration of $-dc/dt=kc^n$ (where n = order, c = concentration, and t = time), provides

$$[1/(n-1)](1/c^{n-1}-1/c_o^{n-1})=kt$$

If the relative concentration (a) = c/c_o and time parameter (T) = $kc_o^{n-1}t$ then the equation rearranges to

$$a^{1-n}-1 = (n-1)T$$

If the fraction reacted (p) = 1-a and $K=kc_o^{n-1}$ then

$$(1-p)^{1-n} \simeq 1+(n-1)Kt$$

which on expansion and disregarding terms >2nd order leads to the approximation

$$t/p = nt/2 + 1/K$$

so that a plot of t/p against t gives a linear relationship with a slope of n/2. Above p = 0.4 the calculation becomes progressively more approximate, but calculation to half an order is assured at all values of p. The rate constant (k) may be calculated from the 1/K intercept. A computer program "PLOTDATA" was written which operated on the data to fit 1st, 2nd, or 3rd order according to the standard equations, and also calculated the order according to Wilkinson, by the relationship above. A least squares fit was achieved using the procedures of Lee and Lee[62] such that

$$\text{slope } (m) = \Sigma X_i Y_i / \Sigma X_i^2$$

$$\text{intercept } (c) = (\Sigma X_i^2 \Sigma y_i - \Sigma x_i \Sigma X_i Y_i)/n\Sigma X_i^2$$

for n pairs of data (x_i,y_i) where $X_i=x_i-\bar{x}$ and $Y_i=y_i-\bar{y}$

and Pearson's correlation coefficient (r) = $\Sigma X_i Y_i / \sqrt{\Sigma X_i^2 \Sigma Y_i^2}$

DISCUSSION.

Figure 4.11 shows the comparison between integral order correlation and that after Wilkinson. It will be noted that, within the accuracy reported (i.e. 0.5 order), the fit after Wilkinson is excellent.

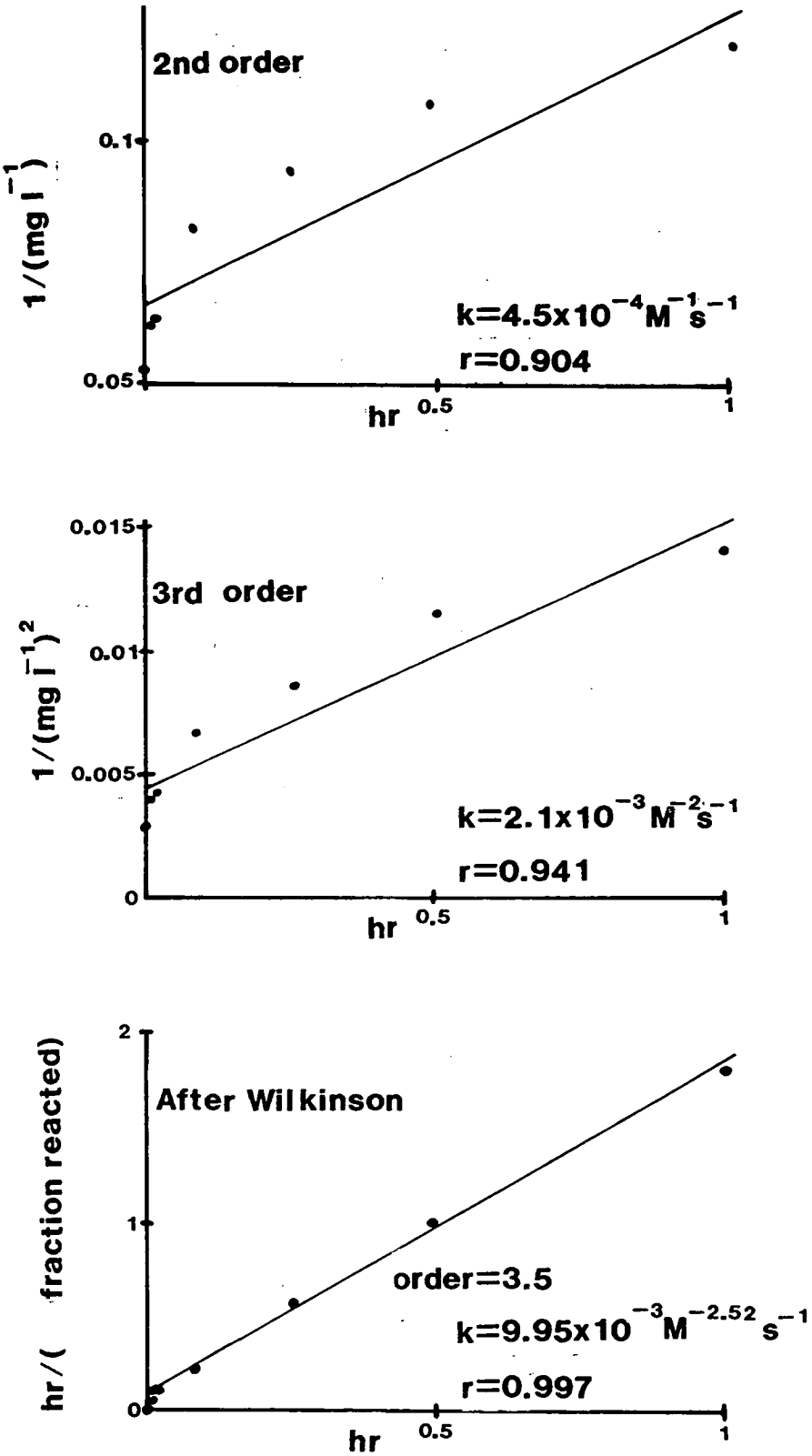


FIGURE 4.11. Kinetics for the loss of aluminium from solution: 1+5 mix of leachate to inlet at 8 °C

Other plots for the fitting of his equation to each determinand over the restricted ranges 0-3 hr and 3-500 hr are summarised in Table 4.12. This arbitrary division appears to be generally appropriate from an examination of the testing at a variety of time ranges.

time	: 0-3 hr		3-500 hr	
ratio	: 1:5	1:10	1:5	1:10
determinand:				
aluminium	3.5 (1)	8.7 (.98)	1.9 (.92)	1.6 (.95)
calcium	2.0 (1)	2.2 (.94)	---	---
silicon	2.7 (1)	3.6 (1)	2.3 (1)	1.8 (.99)
magnesium	2.1 (1)	8.6 (1)	---	---

TABLE 4.12(a) Order of reaction for the precipitation of elements at 8°C. Correlation coefficients in parentheses.

time	: 0-3 hr		3-500 hr	
ratio	: 1:5	1:10	1:5	1:10
determinand:				
aluminium	4.1 (1)	2.9 (1)	1.8 (.91)	4.5 (1)
calcium	2.0 (.97)	2.0 (1)	---	---
silicon	3.0 (1)	2.6 (1)	2.5 (1)	5.3 (1)
magnesium	2.0 (1)	2.7 (1)	---	---

TABLE 4.12(b) Order of reaction for the precipitation of elements at 25°C. Correlation coefficients in parentheses.

The order indicated for each element for a 1:5 mixture of leachate to inlet waters is good for both temperatures and over the two time ranges indicated. However a more uncertain picture is indicated at a ratio of 1:10. At 1:50, because of the small proportion of solids formed relative to elemental concentrations in solution, gave no meaningful data. At a ratio of 1:10 the orders exhibited by the clay mineral-forming elements were different in each reaction vessel. Part of the variability will have been due to the relative inaccuracy of aqueous determinations at low precipitation quantities but the problem of nucleation, rather than co-precipitation with calcite, will have also been a factor.

The rate of calcite formation would be expected to be first order with respect to calcium in an environment of abundant nucleation sites and where carbonate formed the dominant inorganic carbon species, as would be found in Kinghorn Loch. This was found to be the case by Kazmlerczak et al[23] (see Chapter 4.7.1). However the present study indicated second order compliance at 8°C and 25°C for a 1:5 and 1:10 ratio over each time interval within the experiment. These findings are compatible with those reported by Plummer et al[24] for lower carbonate concentrations at near-neutral pH (see Chapter 4.7.1). Reddy[63,64] considered this behaviour (at near-neutral pH) to be due to interfering ions, primarily phosphate, causing surface growth rates to become rate determining and thereby proportional to calcite surface area. Although such interferences, including coating by the formation of clay minerals and by possible inclusion of phosphate, iron and magnesium, are to be expected, the presence of considerable supersaturation with respect of calcite and of abundant calcite surfaces might be expected to limit this effect.

Figure 4.12 plots the elemental ratios of aluminium, silica and magnesium relative to calcium in the precipitate, at all time intervals. The composition of the precipitate was, in this instance, calculated from the aqueous concentrations. It will be observed that there is no indication of fixed elemental ratio co-precipitation with calcite. Figure 4.13 provides a similar treatment for aluminium and magnesium relative to silicon and, while no fixed elemental ratio is indicated, both aluminium and magnesium are significantly enriched relative to silicon at longer time intervals suggesting the presence of mixed layer clay structures (discussed further in Chapter 5.7.3).

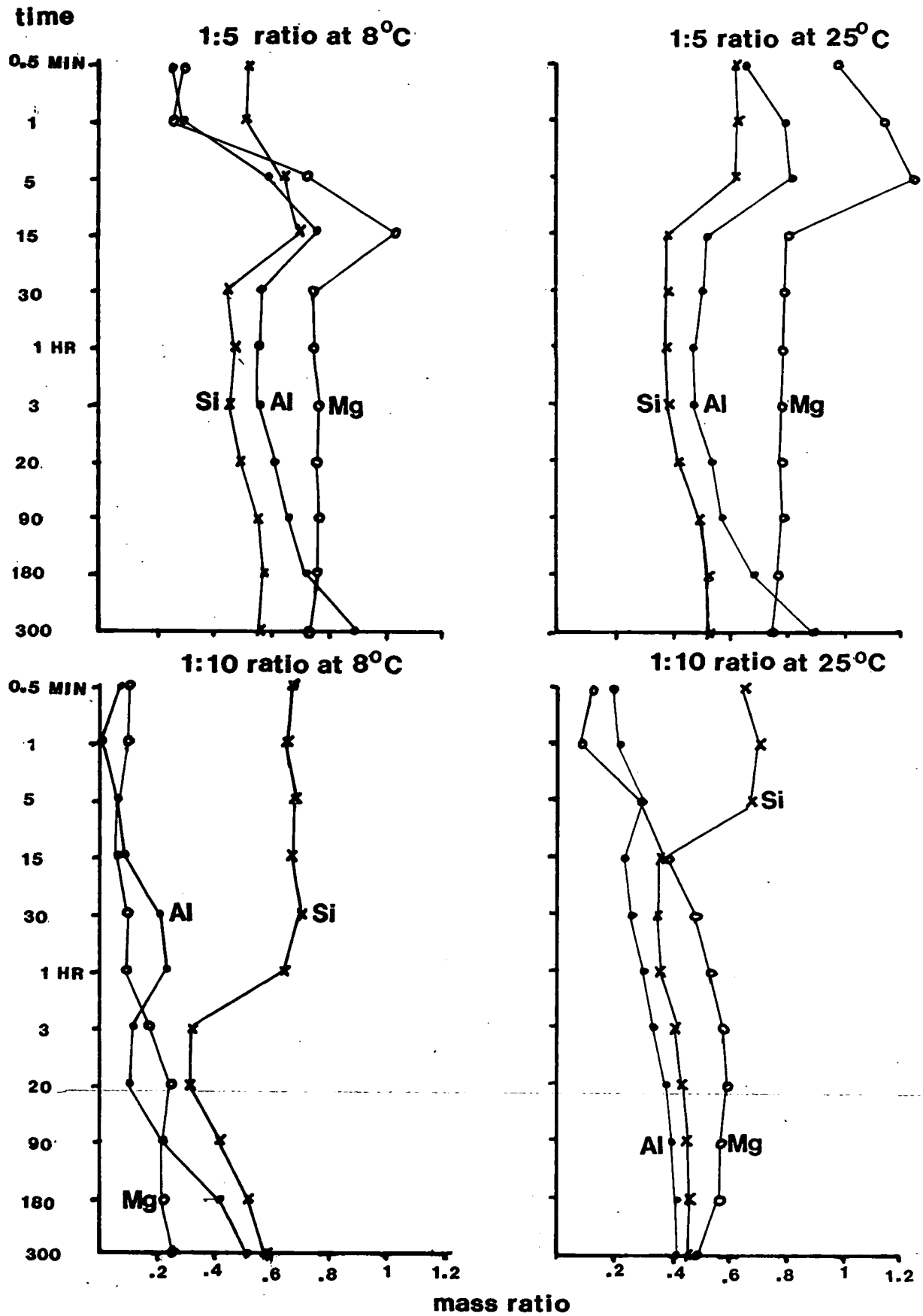


FIGURE 4. 12. Mass ratio of elements relative to calcium

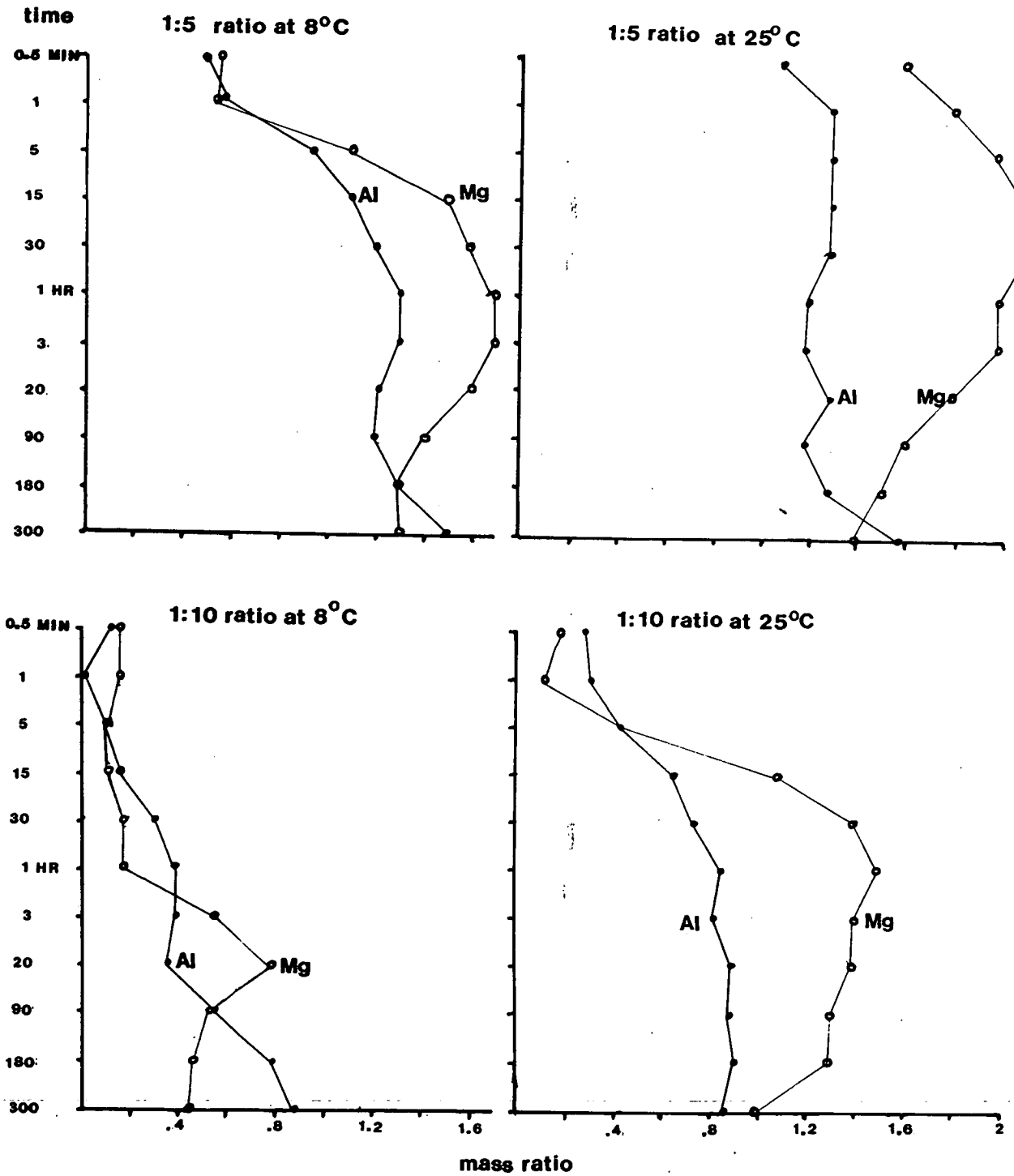


FIGURE 4. 13. Mass ratio of elements relative to silicon

The situation was thus perceived as being complex and, in an attempt to clarify the role of co-precipitation with calcite, further experiments were devised using a thin-film XRF technique to look at the formation of deposits with and without the presence of calcite formation.

4.10.2. COMPOSITION OF PRECIPITATE.

It was considered in Chapter 4.10.1 that calcite formation may play an important, though undefined, part in the precipitation of the other elements. In order to attempt to determine the dependence on calcite formation four sets of samples were prepared. These samples were based on a 1:25 ratio of "combined leachate" (Table 4.7) to north inlet water (equivalent to a 1:7.7 ratio of leachate to Kinghorn Loch:inlet water). One set consisted of these filtered waters in the correct ratio, labelled 'N', while another contained the same chemical proportions except that it was prepared from the individual inorganic chemicals and was labelled 'S'. A third set was depleted in calcium to reduce the calcium level below that needed for calcite formation as indicated by the model with a corresponding reduction in carbonate, labelled 'C'. A final set was additionally depleted in magnesium and carbonate to a level avoiding possible deposition of calcite or dolomite and this was labelled 'D'. The composition of each solution was processed through the speciation model to determine the starter pH that the mixture should be given. Table 4.13 sets out the starter analysis found for each sample type.

Samples were prepared by the slow mixing of up to four dosing solutions using a peristaltic pump. Samples were held in 250 cm^3 polypropylene bottles with unpigmented polypropylene tops. Samples

type : determinand:	'N' & 'S'	'C'	'D'
calcium	1.056	0.001197	0.001197
magnesium	0.7324	0.7324	0.001039
sodium	7.503	7.503	7.503
potassium	0.006767	0.006767	0.006767
chloride	0.971	0.971	0.971
sulphate	0.7499	0.7499	0.7499
aluminium	0.204	0.204	0.204
nitrate	0.8003	0.8003	0.8003
silicon	0.2576	0.2576	0.2576
boron	0.00752	0.00752	0.00752
ammonium	0.01922	0.01922	0.01922
carbonate(*)	2.813	1.591	1.208
bicarbonate(*)	1.627	1.407	1.271
hydroxide(*)	0.8967	0.8613	0.8523
pH(*)	10.46	10.25	10.2

TABLE 4.13. Starter analysis for each sample type (in mM) (*) was determined by speciation model.

were held at 20°C and subjected to vigorous mechanical shaking for ten minutes each day. Three replicates of each sample type and incubation time were prepared and removed from incubation after 1, 2, 25, and 80 days respectively. On removal the samples were vigorously shaken for 30 minutes and placed in an ultrasonic bath for one hour. Three aliquots of 10 cm^3 of each sample (or 1x200 cm^3 for 'D' type) were filtered through moistened polycarbonate membranes (see Chapter 9 for procedure) being very careful to work as cleanly as possible avoiding dust particles and using filtered rinse water. Two lots of 200 cm^3 of the remaining replicate samples (or 1x250 cm^3 for type 'D') were used to determine the suspended solids content. The membranes bore 50-100 ug for types 'N' and 'S' and up to 50 ug for types 'C' and 'D'. These were used for the determination of major elements by the thin-film XRF technique, and Table 4.14 presents the results obtained, quoted as a ratio relative to silicon.

(A) Incubated for 1 and 2 days before analysis.

type : determinand:	'N'	'S'	'C'	'D'
susp.solids	254-271	123-225	134	1-2
aluminium	1.1-1.3	0.65-1.3	1.1-1.1	0.43-0.53
magnesium	2.7-3.2	0.061-2.5	2.1-2.3	0.04-0.085
calcium	2.9-3.7*	0.43-2	0.023-0.057	0.19-0.57
sodium	<0.01-0.046	<0.01-0.11	0.027-0.044	0.16-0.32
potassium	<0.01-0.032	0.014-0.046	0.006-0.021	0.045-0.082

* excluding one outlier of <0.01

(B) Incubated for 25 and 80 days before analysis.

type : determinand:	'N'	'S'	'C'	'D'
susp.solids#	121-146	113-145	61-63	0.4-2
aluminium	0.88-1	0.85-1.2	0.88-1*	0.49-0.71
magnesium	1.6-2.4	1.9-2.5	2.1-2.7**	0.06-0.18
calcium	1.6-2.4	0.24-1.2	0.017-0.13	0.29-0.73
sodium	<0.01-0.045	<0.01-0.052	<0.01	0.16-0.23
potassium	<0.01-0.031	<0.01-0.055	<0.01-0.07	0.046-0.087

* excluding one outlier of 0.54 ** excluding same outlier of 0.69
# loss of material to sides of vessel

TABLE 4.14. Results obtained for the analysis of synthetic samples of loch water. All results as a mass ratio relative to silicon.

It would appear from these results that the formation of clay minerals is independant of the deposition of calcite and that calcium does not form a substantial component of the clay minerals formed. The molal ratio of magnesium:aluminium:silicon was found to be within the range 1.03-1.52:1.9-2.6:1 for 80% of results at all time intervals for natural ('N'), synthetic ('S') and calcium depleted synthetic ('C') samples. The formation of a higher silicon deposit was indicated for some synthetic samples for a 1 day incubation.

Calcite deposition in the synthetic ('S') samples was slower and less complete than in the natural situation. The reason for this is unknown, since humic material, the only component known to be absent

in the 'S' set does not appear to be precipitated in laboratory experiments (Chapter 4.7.1.1) and therefore would not act as a nucleus for calcite formation. The samples that were depleted with respect to calcium and magnesium ('D') gave a negligible deposition of material, and serves to indicate the important role of magnesium in the formation of clay minerals.

CHAPTER FIVE

LOCH SEDIMENTS

5.1. SURFACE SEDIMENTS.

5.1.1. PARTICLE SIZE ANALYSIS.

5.1.1.1. SAMPLING TECHNIQUE.

Samples for particle size analysis were collected during April 1981 with the aid of a small Van-Veen grab with a "bite" of approximately 0.025 m^2 (see Figure 5.1.). The grab proved highly successful except in areas containing stones of a size in excess of 10 mm or where large quantities of macrophyte debris were present. Drake[65] found that Van-Veen, Ponar and weighted Ponar grabs were suitable for sampling particles up to 16 mm in diameter, although the efficiency of the Van-Veen grab was evidently lower, particularly for larger particle sizes. For synthetic samples with a particle size range of 2-4 mm, recovery was 75% whilst at 8-16 mm recovery was 50%. With a thixotropic mud of the kind met in Kinghorn Loch recovery of the larger sizes is likely to be much improved on this figure. Most samples were recovered with a mud surface within 5 mm of the doors in the top of the grab and with a coherent, undisturbed surface (where one existed). Thus for those stations for which results are presented, the samples were considered to be representative. The scoop depth was estimated at 70 mm with a mean depth of 30 mm. This grab was also used for benthos sampling and its suitability for this work will be discussed in Chapter 7.

5.1.1.2. THEORY.

Analysis of the samples for particle size was based on that described by Buchanan[66]. The system relies on a geometric grade scale by which greater emphasis is placed on the separation of smaller sized fractions. Thus grades of sand and silt are conveniently divided into a reasonable number of classes. The classes are formed by the

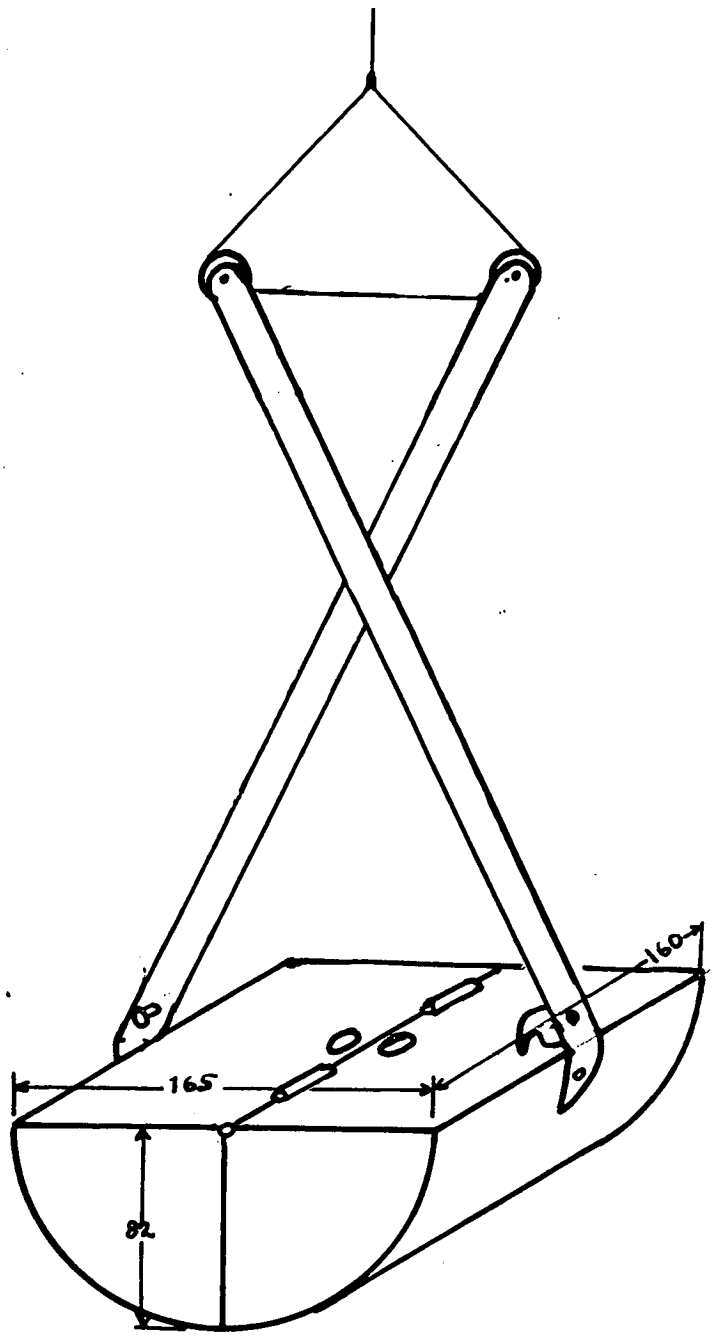


FIGURE 5.1. Van-Veen grab.

logarithmic transformation of Krumbein to give the phi notation where phi= $-\log_2$ of the particle size diameter in mm as shown in Table 5.1.

name		particle size um	phi	name		particle size um	phi
granule		2000-5600	-1	silt	coarse	31-63	+5
sand	v.coarse	1000-2000	0		coarse	15.6-31	+6
	coarse	500-1000	+1		fine	7.8-15.6	+7
	medium	250-500	+2		fine	3.9-7.8	+8
	fine	125-250	+3	clay		<3.9	+9
	v.fine	63-125	+4				

TABLE 5.1. The Relationship Between Spherical Particle Size and Phi Notation.

During the analysis the wet sample was initially split into sand and silt-clay fractions by wet sieving to 63 um. The sand fractions were dried in an oven at 70°C and the silt-clay fraction was further analysed by pipette analysis according to settling velocities provided by Stokes' Law[66]. According to this law the settling velocity in m s^{-1}, V, is given by:

$$V = Cr^2$$

where C = a constant
r = radius of a particle (in m)

and $C = 2(D-d)g/(9z)$

where D = density of the particle (in kg m^{-3})
d = density of water
g = acceleration due to gravity (in m s^{-2})
z = viscosity of water (in kg m^{-1} s^{-1})

By this formula the depth to which particles of a particular size will sink in a given time may be calculated. By taking a sample at this depth and time particles of that size and smaller will be collected. The settlement times used in the analytical procedure (Table 9.9.) are based on several assumptions necessary in order to

make use of the above formula. Particles are considered to be spherical, composed of quartz (D = 2650) and possess no significant attractive forces with regard to other particles. The dilution of the particles in the suspension is considered to be great enough to prevent any physical contact between particles. If the particles are flattened then sedimentation will be much slower and the settlement times shown will capture larger particles.

Buchanan recommends destruction of the organic matter prior to determination of particle size but the analytical procedure used was based on that of the Estuary Survey Section of the F.R.P.B.[67] and does not employ this pretreatment. The organic material in the sediments of the loch is extremely fine and forms an integral part of the structure. Morgans[68] observed that the organic matter acts, as do carbonates, as a binding agent forming stable aggregates. It is the native material, whether or not aggregated, that forms the substrate for invertebrates and therefore stable aggregates should be preserved wherever possible. Some destruction is however inevitable. In order to preserve the natural level of aggregates it would be necessary to maintain the surface charge of particles by careful maintenance of pH and ionic regime and by avoiding any abrasive disturbance during sorting.

The fractionated material was retained for chemical analysis, and in order to provide a reasonable amount of clean material the use of sodium hexametaphosphate as a deflocculent was omitted and the initial sample weight doubled. Further, instead of 20 cm^3 being removed as per the standard method at each time interval, 50 cm^3 was taken. This increased volume removed 12 mm of sample in 5 s using a

modified pipette compared to 5 mm in 7 s by the standard method. 15 cm^3 of the volume will contain material that will be up to 3% oversized by this modification. It was considered that errors due to sample preparation, abrasion of particles during sieving and the quantitative transfer from the dry sieves, were more substantial than errors introduced by the necessary modifications made. Details of the analytical procedure form Chapter 9.4.

5.1.1.3. PRESENTATION OF RESULTS AND STATISTICAL APPRAISAL

The dry weight within each fraction of a sample are best presented in a cumulative percentage frequency curve set against the phi notation. Each sample has been presented in this manner in Appendix B.1 which includes a listing of statistical parameters defined by the following equations.

Mean particle size , $M_0 = (Q_{84} + Q_{16})/2$

where Q denotes the quartile phi-value at the given percentage

Median particle size, $Md_0 = Q_{50}$

Sorting coefficient, $QD_0 = (Q_{84} - Q_{16})/2$

Skewness, $SKq_0 = (Q_{16} + Q_{84} - 2Q_{50})/(Q_{84} - Q_{16})$

Table 5.2. illustrates how these parameters are used to provide a description of the sediment[65].

It will be noted that the majority of the sediments found in Kinghorn Loch are muds, most of a fine nature. Figure 5.2. illustrates this graphically on a plan of the loch. Some samples were not taken either because the stations were found to be over rock or very coarse sediment or because of vegetation. These causes are marked on the plan. Additionally Appendix B.2 carries a comprehensive description of the sediment surface compiled from the visual examination of grab

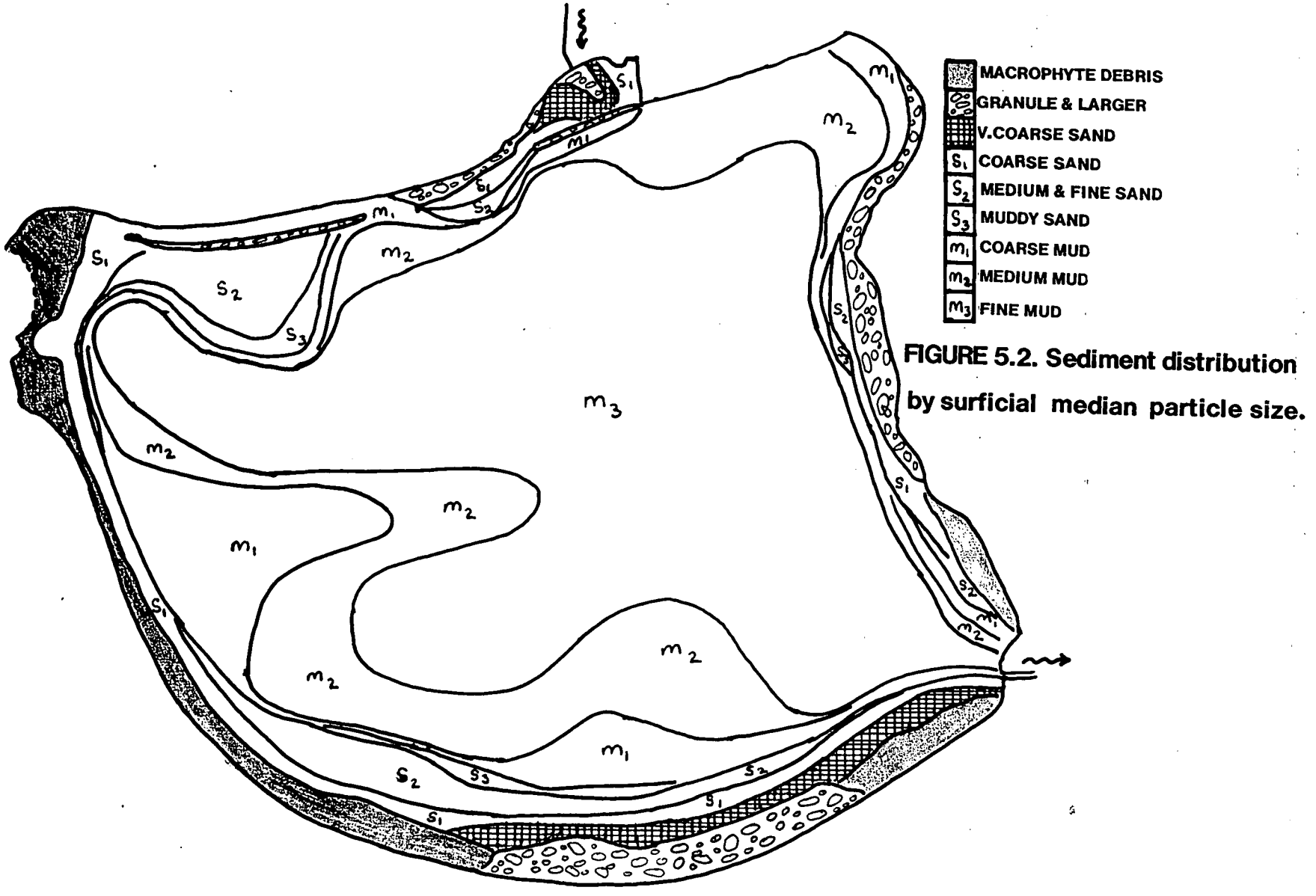


FIGURE 5.2. Sediment distribution by surficial median particle size.

Median in range (phi)	Name
<-1	granule/pebble
-1 to 0	very coarse sand
0 to 1	coarse sand
1 to 2	medium sand
2 to 3	fine sand
3 to 3.75	muddy sand
>3.75	mud

Sorting coefficient	Type
<0.35	very well sorted
0.35 to 0.50	well sorted
0.50 to 0.71	moderately well sorted
0.71 to 1.00	moderately sorted
1.00 to 2.00	poorly sorted
2.00 to 4.00	very poorly sorted
>4.00	extremely poorly sorted

TABLE 5.2. Sediment Nomenclature.

samples, particle size analysis and the sieving and results of invertebrate analysis.

Figure 5.3. plots the moisture content (as a percentage of the wet weight of sediment) which gives an indication of the excessive "wetness" of some of the sediment. Even so, the surveys were taken during February 1981, covering a period of very calm weather. Moisture contents as low as these were not seen again prior to the leachate being removed and between these times a wide band of moisture contents well in excess of 90% developed over sites from Station 39 through 27 and 23 to 21 and from 12 to 14. Only stations in a reasonable depth of water and off the direct line from leachate to deep water retained 1981 levels (stations 16 and 35). In particular, in the vicinity of station 39, resuspension of sediments led to extremely liquid mud held over some 1 m of the water column and apparently involving the reworking of the upper 0.1 m of the settled

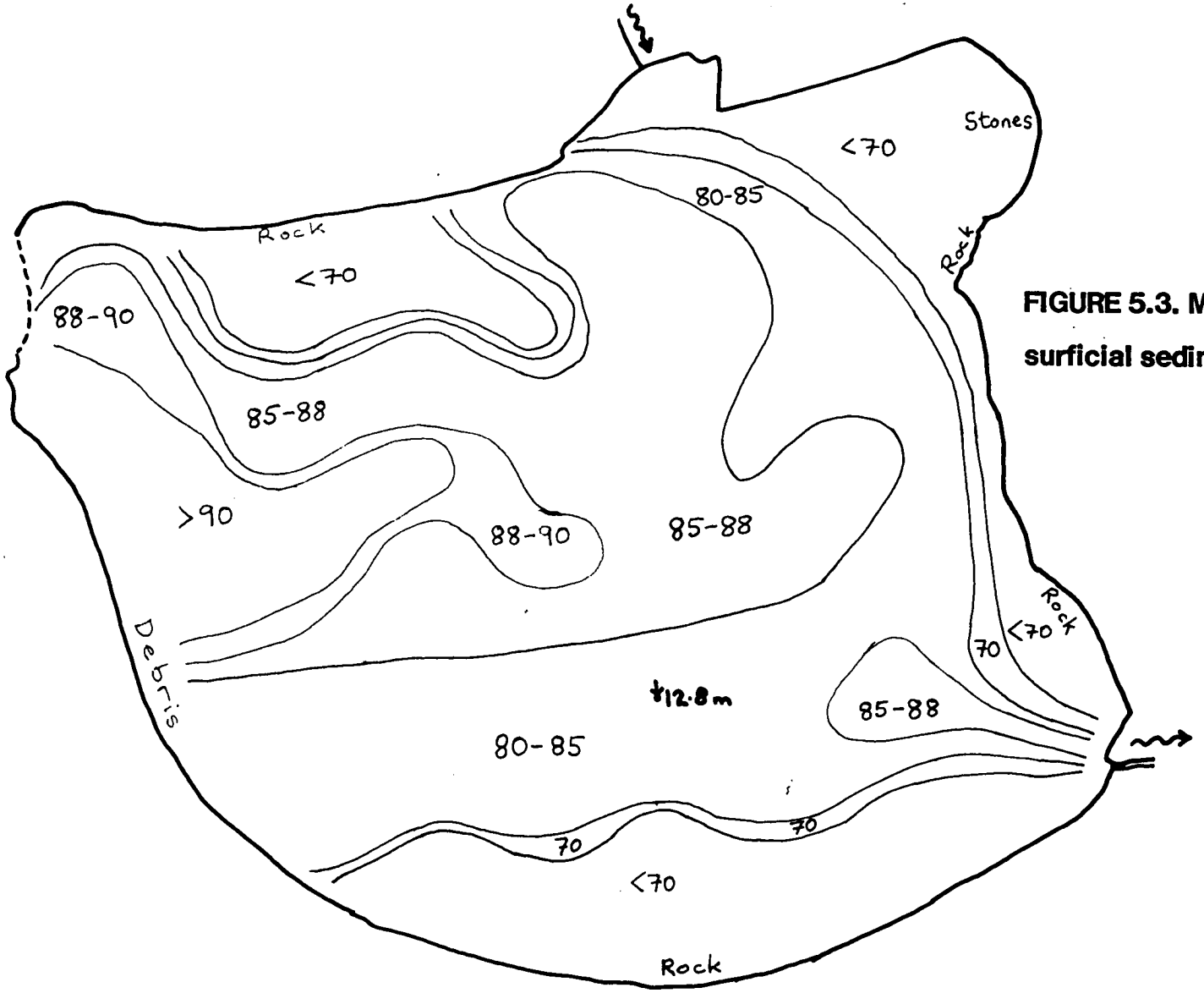


FIGURE 5.3. Moisture content of surficial sediment (% wet weight).

mud. The pH value of the loch at this time was pH 9.6. It was observed that resuspension becomes more persistent at higher pH. Since the diversion of the leachate in May 1983 and the subsequent lowering of the loch pH reworking of the sediments has been followed by a rapid settlement and return to clear water conditions.

In order to investigate the effect of pH and ionic strength on settlement rate, 150 g of wet sediment was suspended in 10 l distilled water. Representative sub-samples were transferred to 1 l plastic bottles and the pH adjusted from the initial pH 8.6 to give two sets of sub-samples at pH values of 7.5, 8.6, 9.5, and 10.5 by the addition of 1 M sodium carbonate solution or 1 M sulphuric acid as required. The electrical conductivity of the sample at pH 10.5 was measured to be 1280 mhos cm^{-1} and one set of sub-samples was adjusted to this conductivity with 1 M sodium sulphate solution. Each bottle was rolled at 1 revolution s^{-1} for 30 min and adjustment made for any slight change in measured pH. Thus one set presented a range of pH values at constant ionic strength while the other set gave a range of pH values at "natural" ionic strengths. Each bottle was inverted several times and rapidly poured into an Imhoff's glass settlement cone. 50 cm^{-3} was removed from half-depth of water using a bulb pipette with an enlarged jet orifice and passed through a weighed glass fibre disc (grade C). The disc was dried, and reweighed to ascertain suspended solids content. Figure 5.4 illustrates the results obtained at pH 10.5 and pH 7.5. Samples at pH 8.6 gave similar results to pH 7.5 whilst those at pH 9.5 were intermediate. Constant ionic strength samples gave a higher level of residual solids than "natural" samples at the same pH. After 20 hours the supernatant water was carefully removed by syphonage and

any residual water that formed on the underlying sediment was taken off with a Pasteur pipette. The wet sediment was transferred to a weighed polypropylene jar, weighed, and then dried to constant weight at 95°C. The following moisture contents were observed at each pH.

pH	moisture (%) "natural" I.S.	moisture (%) constant I.S.
7.5	95.8	96.7
8.6	96.2	96.7
9.5	96.7	97.3
10.5	98.1	----

TABLE 5.3. Moisture content of sediments found during settlement rate experiments.

These values indicate that the sediment, for an equivalent weight of dry matter, was more than twice as voluminous at pH 10.5 as at pH 8.6 for a "natural" situation and only slightly less so for constant ionic strength. Core profiles contained in Appendix C illustrate this point if comparison is made of the depth of red+red/brown sediment in the two 1983 cores with that taken in 1985. From Figure 5.4 it will be observed that settling times were four times as rapid at pH 7.5-8.6 than at pH 10.5 and while the samples at pH 7.5 contained less than 10 mg l^{-1} suspended solids after 20 hours and appeared clear, that at pH 10.5 retained 34 mg l^{-1} (and 28 mg l^{-1} at pH 9.5) and was distinctly turbid. Thus under the normal conditions of wind and current turbulence the loch water at pH 9.5 and above would be extremely slow to clear. The dominant mineral present in the sediment has been found to be calcite and the observations are consistent with the zero charge point of calcite which is at pH 8.2 (Stumm and Morgan[8]), the mineral surface bearing negative charge above this pH.

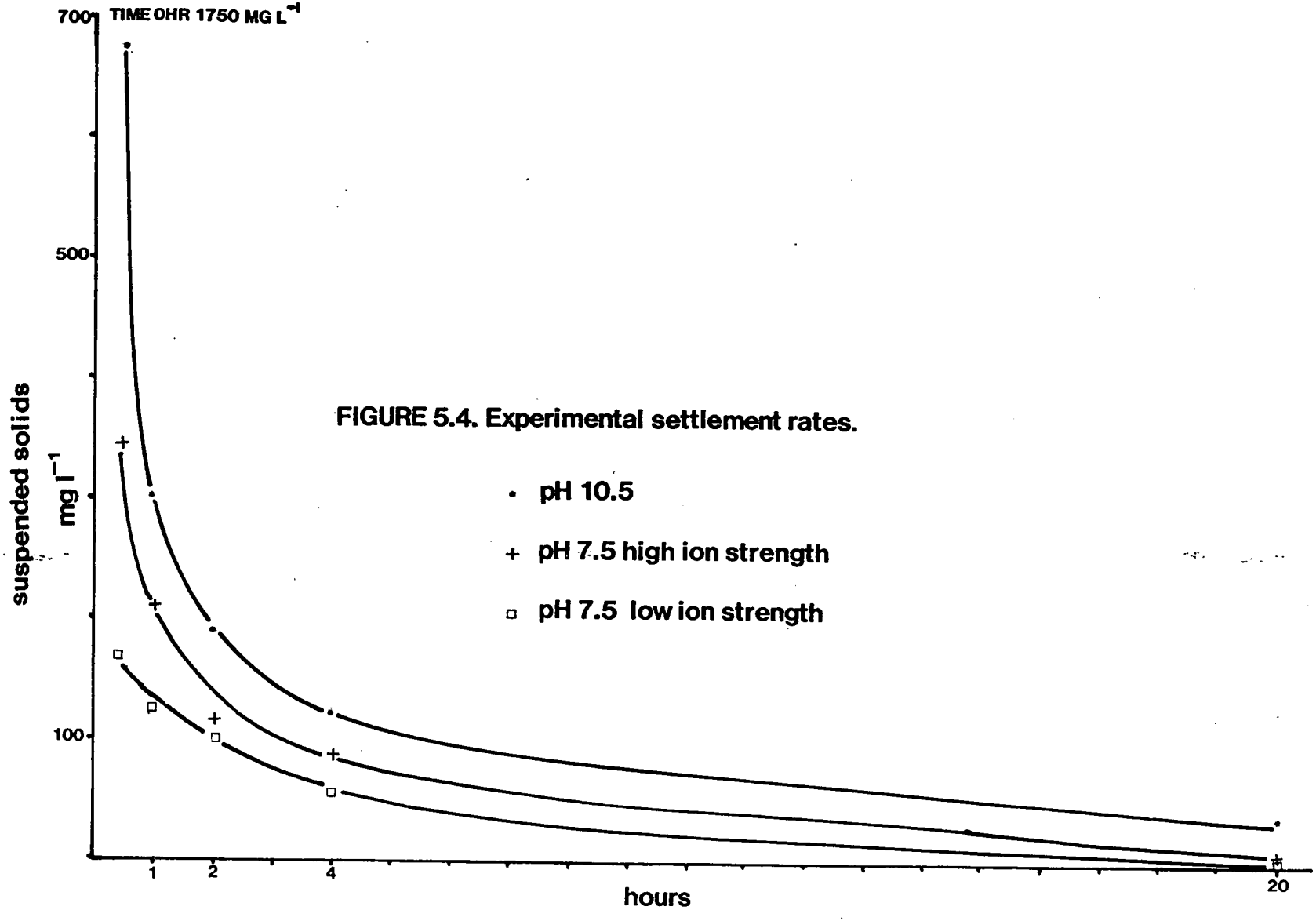


FIGURE 5.4. Experimental settlement rates.

5.1.2. CHEMICAL ANALYSIS OF SURFACE SEDIMENTS

Sub-samples produced during particle size analysis were retained for chemical analysis in order to attempt to determine the tendency for elements to be concentrated in particular size ranges. It was decided to concentrate efforts on three stations, these being 14, 39 and 45. Station 39 was immediately adjacent to the entry point of the leachate while station 45 was the nearest point to the north inlet entry that did not dry out in the summer. Station 14 was chosen as it was the deepest point in the loch.

Each class size was analysed for major elemental components by X-ray fluorescence spectrometry using a fused disc procedure outlined in Chapter 9.2.1.1 and for carbon, nitrogen and hydrogen by elemental analyser as given in Chapter 9.3. Results so obtained for major element analysis required an initial correction for loss on ignition at 1100^{o}C. Ashed values from C,H,N determinations required adjustment for ashing at 475^{o}C before the calculation of volatile and refractory components. Analysis for C,H,N required 30 mg of sample while major element analysis required 1 g. Insufficient sample was available for full analysis, even with the weight proportional pooling of classes, and results were therefore not available for some classes representing minor size constituents.

Little variation in composition was observed for classes of phi5 (<31 um) and finer at stations 39 and 45, while class phi4, the only other class present in significant quantity, showed an appreciable enrichment in silica, as would be expected from an increasing proportion of detrital quartz (sand). The comparison of classes for these stations is shown in Table 5.4 illustrating the analysis results for class

phi4 and the mean and range of results for classes phi5 to 9.

(a) Station 39.

size class	size (um)	% SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5
4	125-63	14.9	5.28	3.03	3.42	28.8	0.63	0.27	0.28	0.03	0.28
5-9	<63										
	result	7.75	10.1	4	9.14	21	1.61	0.19	0.34	0.06	0.58
	range	0.1	0.11	0.14	0.15	0.1	0.12	0.01	0.01	0	0.06

size class	size (um)	% inorg C	org C	inorg N	org N	refract H	volatile H
3	250-125	2.34	4.98	<.1	0.21	0.41	0.96
4	125-63	4.92	5.46	<.1	0.34	0.47	1.29
5-9	<63						
	result	4.88	5.65	<.1	0.31	0.47	1.58
	range	0.18	0.42	<.1	0.06	0.02	0.41

(b) Station 45.

size class	size (um)	% SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5
4	125-63	25.3	8.81	4.93	4.98	18.4	0.42	0.38	0.56	0.09	0.33
5-9	<63										
	result	16.8	9.63	3.11	5.45	22.3	0.51	0.29	0.44	0.1	0.36
	range	0.05	0.04	0.28	0.54	0.08	0.06	0.01	0	0.01	0

size class	size (um)	% inorg C	org C	inorg N	org N	refract H	volatile H
2	500-250	6.7	3.65	<.1	0.42	0.27	0.65
4	125-63	4.32	6.64	<.1	0.64	0.43	1.24
5-9	<63						
	result	5.06	6.49	<.1	0.72	0.49	1.25
	range	0.12	0.13	0.3	0.31	0.02	0.22

TABLE 5.4. Chemical Analysis of Particle-Sized Surface Sediment for Stations 39 & 45, with range of results for silt/clay fraction.

At station 14 the bulk of the sediment lay within class phi7 and coarser and major element analysis was not possible for classes phi8 and 9. However it was possible to obtain major element analysis on station 21 for these classes and it was hoped that since these stations are in a similar environment that the analyses could be compared. Unfortunately station 21 proved to possess significantly

more silica and comparison was not possible. Table 5.5 illustrates the full results for station 14. Since there appeared to be a distinct gradation of C,H,N results through the classes it proved possible to split the composition into discrete class boundaries between phi5 and 8 from the composite results by use of the formula:

$$P_F = P_f(100-W_f)-P_{f+1}(100-W_{f+1})/(W_{f+1}-W_f)$$

where P_F = percentage of element within class boundaries of f
P_f = percentage of element within class f to phi9
W_f = cumulative weight percentage of class phi-2 to f

For an even distribution of weight fractions errors involved would be similar to those on the actual results. However, since most of the sample mass was concentrated in one fraction only, errors become correspondingly more significant. Table 5.5 includes estimates of these errors using standard deviations contained in Chapter 9.3. No attempt was made to compensate class phi6 to 7 for major elements contained in class phi8 to 9 as class phi6 to 7 contained 93% of material and conjecture on the composition of class phi 8 to 9 would have generated greater uncertainty.

Analyses at each class/pooled classes were accumulated to ascertain the proportion of sample mass accounted for by the determinands used. Due to the incompleteness of the data this was possible on six sets only. Major elements were accumulated as the oxide percent and inorganic C as CO_2 for carbonate incorporation. Organic C was assumed to be associated in the proportion CO as a generalised ratio for freshly degrading organic matter taken as carbohydrate. Organic N and H were considered accounted for within this C:O organic ratio. Refractory H (not volatilized at 475°C) was accounted as H_2O held in mineral lattice. Table 5.6 illustrated the accumulations obtained

and show mean accountability for 98.8% of material.

(a) Major Elements

size class	size (um)	% SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5
2/3	500-125	18.4	8.55	2.63	4.99	20.5	0.28	0.24	0.32	0.07	0.43
4/5	<125	14.9	9.5	2.54	5.44	20	0.37	0.23	0.32	0.07	0.44
6	<31	13	11.4	2.37	6.96	30	0.5	0.19	0.3	0.08	0.55

(b) Cumulative C,H,N Results

size class	size (um)	% inorg C	org C	inorg N	org N	refract H	volatile H
5	<63	5.8	6.91	<.1	0.6	0.52	1.23
6	<31	6.14	6.32	<.1	0.65	0.65	1.14
8	<8	2.2	10.15	<.1	1.03	0.88	2.57
9	<4	1.18	10.62	<.1	1.23	0.83	1.97

(c) Carbon Results for Discrete Classes (c.l. at 95%)

size class	size (um)	% inorg C result	inorg C c.l.	% org C result	org C c.l.
6/7	31-8	6.48	0.36	5.99	0.72
8	8-4	3.35	0.08	9.62	0.8
9	<4	1.18	0.04	10.62	0.3

TABLE 5.5. Chemical Analysis of Particle-Sized Surface Sediment for Station 14 for majors and C,H,N with class split of C results. Note: classes pooled on weight proportional basis (phi<6)

station	size class	size (um)	% accumulated	station	size class	size (um)	% accumulated
14	4/5	<125	95.2	39	4	125-63	98.2
14	6	<31	111.0	39	5	<63	90.6
				45	4	125-63	99.9
				45	5	<63	98.0

TABLE 5.6. Percentage of sediment material accounted for by analysis applied.

Aluminium and magnesium are seen to increase proportionally at all stations at finer size classes, indicating a higher proportion of clay minerals while silica, presumably the detrital quartz portion, decreases with decreasing class size. Note that these coarser

classes constitute a minor part of the whole. For all stations calcium was present at higher levels in the silt/mud fraction but only station 14 showed any gradation within this fraction. Station 14 exhibited a calcium maximum of <31 um and, judging from the inorganic carbon results, would show a maximum calcium carbonate level for the size range 31-8 um, finer particles than this becoming increasingly deficient in inorganic carbon. Stations 39 and 45 showed a similar calculated calcium carbonate percentage of 37.5 and 39.8% respectively while station 14 showed 48%.

Proportional changes in the organic component are not evident at stations 39 and 45 for the silt/mud fraction but station 14 shows a gradual enrichment in organic carbon and nitrogen toward finer particle-sizes and shows an organic level generally higher than the other stations. Atomic ratios of organic carbon: organic nitrogen for phi5 and smaller at station 14 was C/N = 13.4, at station 39 it was 21.3 and 10.5 at station 45. Hakanson[69] (and others) gives a planktonic ratio for lakes of approximately 5.6, while data presented by Gjessing[70] and Golterman[71] indicate ratios of 10-20 for aquatic humus material. These ratios suggest that the organic component found at station 39 [9.7% of gross sediment dry weight as C_2H_2O + xN (ratio given by Gjessing)] is principally derived from humus material entering with the leachate with, perhaps, a detrital component from bank erosion to the north. Station 45 would be least affected by the material from the leachate, while both 14 and 45 would receive a significant planktonic input. Organic components at 14 and 45 (assuming a medial composition of $C_{1.5}H_2O$) would be 14.4% and 13.7% of the gross sediment dry weight respectively.

5.2. TAKING OF SEDIMENT CORES

In order to further investigate the fate of material deposited within the loch it was necessary to obtain profiles through the sediment, preferably to a depth representing conditions prior to the ingress of caustic leachate. The following aims were identified.

(1) To determine the depth and quantity of material deposited since pollution began.

(2) Date, by radionuclide analysis, any horizons within the core and determine the degree of reworking of the sediments.

(3) Provide a sedimentation rate for "natural" conditions in the loch and compare this with recent deposition rates.

(4) Determine the redox environment and investigate the relationship between chemical parameters of the core material and accompanying interstitial waters.

(5) Attempt to identify mineral forming processes within the profile.

5.2.1. DESIGN AND OPERATION OF CORER.

Initially a simple corer was designed to obtain profiles from shallow water near station 39. This corer proved successful even when sampling very liquid muds to the south of the leachate inlet pipe. In the event, assistance was offered by members of Fife Sub-Aqua Club and their kind help is most gratefully acknowledged. The corer did not require significant modification for use by a diver.

The corer is illustrated in Figure 5.5 and consisted of a 2 m length of 100 mm diameter PVC pipe bevelled at the lower end to ease entry into the sediment. Inside this pipe was placed a flexible, heavy-

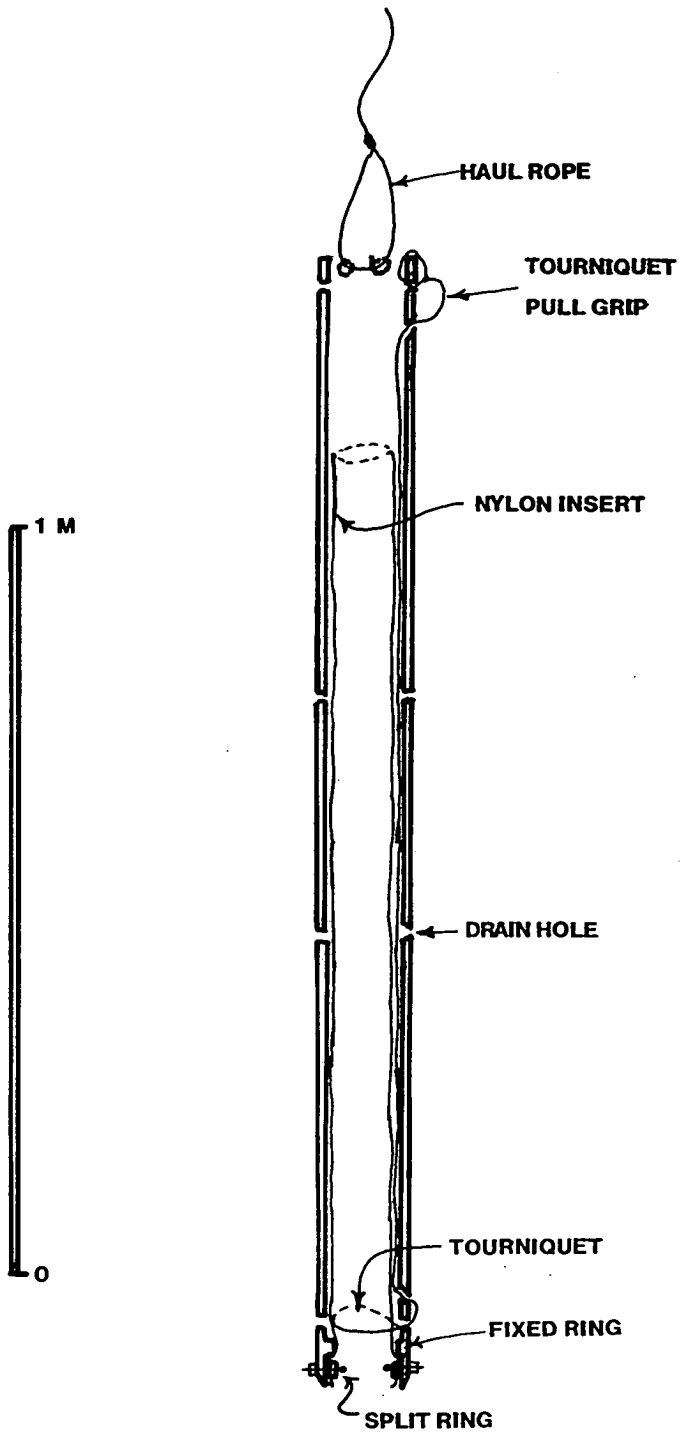


FIGURE 5.5. Corer.

gauge nylon tube (150 mm wide when flat) of the sort used for preparing heat-seal bags. The tube was marked on the outer side with divisions at 30 mm intervals. It was held at the lower end by a split-ring-clip made from a 20 mm length of the pipe, with a segment of the circumference removed so that on insertion inside the nylon tube of the corer the width of the split was 1-2 mm only. This fitted against a similar piece of pipe sealed to the inside of the corer. The clip was held in place by three bolts passing through it and the corer body. Nylon cord entered the corer pipe 75 mm from its lower end and looped loosely about the nylon tube. It re-entered the pipe 25 mm higher and re-emerged near the upper end of the pipe in a hand grip. When retrieving the core this line was pulled to form a tourniquet about the lower end in order to hold the soft mud of the core. Once pulled the weight of the core prevented it loosening. The corer was equipped with retrieval cords near the base and near the top, and a substantial pulling grip over the upper end of the device.

The corer could be used in water depths to 4 m by the use of a 3 m additional length of pipe attached to the corer, and cores were retrieved by this means from stations 7, 39 and 45. The SCUBA divers retrieved cores in July 1983 during a severe phytoplanktonic bloom which required them to work blind. Even so, the apparatus was readily employed and the tourniquet cord could be fixed at the top so as to be easily found. All cores obtained with this device incorporated a substantial depth of dark, fibrous material, being the "natural" sediment, below the polluted deposition.

Appendix C illustrates in graphical form the physical characteristics of each of the sediment cores profiled.

After taking a core the clip was removed and the tourniquet replaced with a secure knot. The core was lifted through the pipe and tied securely well above the sediment surface. The nylon tube was suspended vertically and the upper tie removed. The undisturbed sediment could then be probed at progressive intervals for Eh determination or segmented into polythene bags.

5.2.2. PREPARATION OF CORE SEGMENTS FOR ANALYSIS.

Eh measurements (Chapter 5.3.) indicated that sediments existed within a reducing environment and it was therefore necessary to determine interstitial water chemistry in such a way as to prevent oxidation. Attempts had been made to recover interstitial water from a core taken from station 26 in March 1983, by use of pressure filtration (squeezing) with oxygen-free nitrogen but this proved unsuccessful. Analysis for reactive silica and sulphate had been possible on water combined from segments and these results will be considered later. The muds, even if apparently very wet, were thixotropic and yielded very little water. Rowlatt[11] using a pressure of 3.4×10^5 N m^{-2} successfully extracted water from cores retrieved from lakes in the Lake District, but for the present cores a pressure of 6.9×10^5 N m^{-2} failed to retrieve more than 1-2 cm^3 of sediment held water. It was reluctantly accepted that the segments could not be kept at sampling temperature for the removal of interstitial water and they were subjected to rapid deep-freezing in order to preserve them. It was found that on thawing out pressure filtration at 3.4×10^5 N m^{-2} (3.4 bar) with oxygen-free nitrogen easily retrieved

sufficient interstitial water for analytical needs. All segments were stored in a deep-frozen state until required for analysis.

Thus the following procedure for segmentation and preparation was employed.

Segments were undisturbed prior to being removed from the core and rapidly transferred to the heavy-gauge polythene bags in which they were to be frozen. The pH of each segment was recorded. The samples were gently worked and the bags sealed so as to exclude air and the bags retained in a cooled box prior to freezing within 1-6 hours. Oxygen diffusion through the polythene skin of the bag prior to deep-freezing should not have been significant. Some early cores recovered for solid component analysis only were deep frozen intact and segmented in a frozen state. This was found to be unnecessary and all subsequent cores were treated as described above.

Samples were required for major and trace element, and C,H,N elemental analysis. Additionally material was needed for radio-dating and XRD crystallography studies. It was also hoped to retain sufficient sediment for scanning electron microscopy and electron microprobe studies (which do not form part of this thesis). Interstitial water was also required. The segment volume was approximately 250 cm^3 with a dry residue component of up to 40 g. Pressure filtration recovered up to 120 cm^3 of water per segment and a minimum of 60 cm^3 was required for analysis. It was considered undesirable to allow samples destined for freeze-drying to thaw and so it was decided to use certain cores for interstitial water analysis and others for matrix analysis, relying on pH profile and visual examination for

core comparability.

Core segments for matrix examination were treated as follows. Deep-frozen segments were placed between heavy gauge polythene sheet and immediately broken up with a metal bar. The broken pieces were divided in half (there being insufficient freeze-dryer capacity to dry the whole) and one part transferred immediately to a 500 cm^3 round-bottomed flask fitted with a B34 cone, and freeze-dried. After freeze-drying the residue was transferred to a polypropylene jar and stored in a cool, dark place. An aliquot of approximately 100 mg was transferred to a small cup formed from aluminium foil, weighed, and dried at 105°C. After cooling the cup was reweighed. Freeze-dried samples were found to contain 0.6-1.8% moisture volatile at 105°C. Freeze-drying should present a gentle technique relative to oven-drying for the investigation of matrix chemistry. It has the advantage of remaining within a solid phase whereby loss of gases do not affect the aqueous based equilibria. Freeze-drying was chosen so as to allow, as far as possible, the maintainance of hydrated mineral species which may otherwise be significantly affected by heating. It is also a technique that keeps the reducing nature of the sediments and thereby protects certain minerals. The remaining part (retained for less heat-sensitive parameters) was transferred to a weighed polypropylene jar and reweighed. It was allowed to thaw and dried to constant weight at 70°C. The final weight was used to determine moisture content and the jar stored in a dark place.

Core segments destined for interstitial water analysis were similarly broken up and the whole sample rapidly transferred to a 500 cm^3 flask (B34 cone) fitted with a purge of oxygen-free nitrogen and allowed to

thaw at 4°C. Thawed samples were transferred to a pressure filtration apparatus (previously purged with oxygen-free nitrogen) incorporating a glass-fibre pre-filter and 0.1 um membrane filter. Pressure filtration at 3.4×10^5 N m^{-2} provided 100 cm^3 "interstitial" water at a mean rate of approximately 10 cm^3 min^{-1}. The filtrate stream was sub-sampled direct, sub-samples being collected for sulphide, anions and metals analysis in that order. A 20 cm^3 glass vial containing 0.25 cm^3 zinc acetate solution was filled with filtrate and 0.25 cm^3 sodium carbonate solution added (see Chapter 9.1.1.1.). The stopper was inserted and the vial inverted several times. This sub-sample was retained for sulphide analysis by the DPD procedure of Chapter 9.1.2.4. A 60 cm^3 polythene bottle was allowed to completely fill with filtrate and the pH recorded before being placed in storage at 4°C. Between determinations the probe was retained in buffer at 4°C and prior to use washed with water at a similar temperature. Approximately 20 cm^3 of filtrate was allowed to flow into a 60 cm^3 polythene bottle containing 0.8 cm^3 concentrated hydrochloric acid. This sample was retained for metals analysis. The pressure filtration was continued until a flow of less than 1 cm^3 min^{-1} was obtained. The filtrate so collected was stored at 4°C and the residue dried at 70°C for possible future use.

The adoption of this procedure presented two separate problems which must be considered in assessing the effect on the chemical composition of the interstitial waters.

(1)Oxidation-reduction.

Several workers have been concerned with the oxidation-reduction

balance within the water both from the effect of squeezing and of exposure to atmospheric oxygen. Troup et al[72] found that the squeezing of anoxic mud gave a steadily increasing concentration of Fe^{2+} in the filtered water up to a certain maximum (3-11 mg l^{-1} in experiments). Davison et al[73] investigating a procedure for the direct analysis of Fe^{2+}, Mn^{2+} and S^{2-} by in situ polarography found that deliberate exposure to atmosphere by stirred aeration reduced Fe^{2+} (initially 0.1 mM) by up to 80% and reduced S^{2-} to undetectable levels. The authors concluded that as the rate of oxygen uptake was insufficient to account for the changes, re-equilibrium with the solid phase was more significant, and that the process was not necessarily linked to oxidation, loss of CO_2, or change in pH value. The effect of squeezing was variable with agreement between in situ sediment pH and extracted water pH being + 0.06 units for Esthwaite Water and +0.3 units for Rostherne Mere. Lyons et al[74] investigated oxidation effects on anoxic carbonate sediments, as significant effects had previously only been reported in iron-rich clastic material. They determined that an effect occured above 0.1 mg l^{-1} dissolved iron but not below this figure. They also observed that references which cited dissolved iron in anoxic sediments but where atmospheric exposure was allowed presented values in the region of 0.1 mg l^{-1} indicating the possibility of this being a neo-equilibrium concentration (presumably with surface deposited FeS). It was also found that the loss of iron was associated in the ratio 1:0.45 with the loss of phosphate. It was postulated that this was an indication of the scavenging potential for orthophosphate of freshly formed $Fe(OH)_3$. It is considered that, during the present study, sufficient precautions were taken with the handling of samples to have maintained a reasonable level of reductive atmosphere throughout.

(2)Freezing.

It was noted that Davison et al[73] considered that mechanical effects of aeration were more important than oxygen in affecting interstitial water chemistry, and it is therefore likely that a fundamental change such as freezing will have a considerable effect on the chemistry. pH was the only parameter to be determined on both the in situ sediments and the extracted water and the results proved to be variable. Table 5.7 lists pH values found for cores at stations 12, 16 and 35 taken during July 1983. Agreement was found to be reasonable in the upper part of the cores and less so in the lower areas where the pH was generally 0.1-0.4 units above the direct sediment measurement. For comparison results are included for a sediment core from station 39 taken during April 1985. A similar pattern is seen except for the surface material (0-30 mm) when the extracted water pH was 0.2 units above the sediment pH and 0.4 units above that in the overlying water.

Reference to the Eh values (Chapter 5.3.) shows that during April 1985 the surface sediments were not under reducing conditions and a nitrogen purge of the oxygen contained in the segment may be responsible for this deviation. Examination of the results obtained for interstitial chemistry (Chapter 5.5.) show differing levels of iron at various horizons and do not support any re-adjusted equilibrium theory similar to that proposed by Lyons et al[74]. Table 5.8 compares the results obtained by direct filtration of core 26 in March 1983 with those given by a freeze-thaw process on core 12 in July 1983.

Unfortunately these stations are very differently situated as station 26 is profoundly affected by leachate.

Segment (mm)	(Station 12 - July 1983) in situ pH	extracted pH	differ -ence	(Station 16 - July 1983) in situ pH	extracted pH	differ -ence
0-30				9.69		
30-60	9.28	9.24	-.04	9.35	9.35	0
60-90	9.2	9.2	0	9.28	9.26	-.02
90-120	9.03	9	-.03	9.15	9.09	-.06
120-150	8.73	8.66	-.07	9	9.02	+.02
150-180	8.51	8.52	+.01	8.98	8.98	0
180-210	8.14	8.14	0	8.88	8.86	-.02
210-240	7.92	7.8	-.12	8.54	8.53	-.01
240-270	7.9	7.96	+.06	8.17	8.29	+.12
270-300	7.69	7.54	-.15	7.72	7.79	+.07
300-330	7.83	7.86	+.03	7.72	7.81	+.09
330-360	8.02	8.2	+.18	7.53	7.41	-.12
360-390	7.69	7.77	+.08	7.8	7.65	-.15
390-430	7.66	7.86	+.2			

Segment (mm)	(Station 35 - July 1983) in situ pH	extracted pH	differ -ence	(Station 39 - April 1985) in situ pH	extracted pH	differ -ence
0-30				8.3	8.5	+.2
30-60	9.34	9.36	+.02	8.8	8.8	0
60-90	9.4	9.38	-.02	8.9	8.9	0
90-120	9.31	9.27	-.04	9.1	9	-.1
120-150	9.12	9.14	+.02	9.1	9.1	0
150-180	9.12	9.1	-.02	9	9.1	+.1
180-210	9.04	9.08	+.04	8.8	8.9	+.1
210-240	8.24	8.34	+.1	8.4	8.5	+.1
240-270	8.02	8	-.02	8.1	8.2	+.1
270-300	7.74	7.93	+.19	7.8	8	+.2
300-330	7.68	7.79	+.11	7.6	7.9	+.3
330-360	7.66	7.91	+.25	7.6	7.8	+.2
360-390	7.86	8.1	+.24	7.4	7.5	+.1

TABLE 5.7. Comparison of pH values down 4 cores showing the difference between in situ sediment pH and filtrate pH after freeze-thaw.

Results for station 12 show similar levels of sulphate in the upper part of the core but twice as much in the lower core. Conversely silica is initially lower but becomes comparable at deeper levels. Unfortunately it is very difficult to estimate the effect of differing pH and redox conditions on these sites but since results were of similar order it would indicate that the effect of freezing segments is not devastating.

date taken:	March 1983			July 1983	
	Station 26			Station 12	
depth (mm)	SiO_2	SO_4	depth (mm)	SiO_2	SO_4
200-250	6.8	114	120-150	3.3	87
250-300	5.2	123	150-180	3.6	101
			180-210	3.9	115
450-550	10.3	108	210-240	4.2	201
			240-270	4.7	261
650-675	9.4	136	270-300	3.8	215
			300-330	7.8	188
675-700	18.1	94	330-360	15.6	179
			360-390	21.2	169
	mg/l SiO_2	mg/l SO_4		mg/l SiO_2	mg/l SO_4

TABLE 5.8. Comparison of analytical results obtained by immediate pressure filtration (station 26) and after initial freezing (station 12). ~~~~~~ is division of red sediment and dark fibrous sediment.

The freezing process evidently caused considerable aggregation of fine mud particles in the sediment and will have had a profound effect on surface area and surface electrical charge available for absorption processes. Alkalinity does not appear to have been modified to any significant degree or in any consistent manner. The effect on pH seems to have been no more dramatic than could have been expected by prolonged squeezing. Given the lack of reported investigations on freezing effects, and as time was not available to follow up these problems, attempts were made merely to standardize technique in order to present information which was comparable within the loch system.

5.3 Eh MEASUREMENT.

5.3.1 THEORY AND LIMITATIONS.

The measurement of Eh as a means of defining the oxidation-reduction potential of a sediment has been used extensively. However, many

workers now recognise that severe limitations are placed on data interpretation. Whitfield[75] has identified several problems which preclude the use of the measurement on an absolute basis and has suggested ways of overcoming those that result from the methodology. The calomel electrode, used as a standard reference, can generate a spurious potential between the liquid junction and test solution, due to the effect of flocculent suspended matter. This interference was reduced by the use of 3.5 M potassium chloride rather than a saturated solution (Whitfield[76]). However the other recommended precaution, that of presenting a remote junction was not incorporated in the electrode used for this study. Similarly the reduction in salt concentration, reduces the hysteresis effects of over/under-saturation due to lower temperatures in the sediment core. Other operational difficulties involve the possible formation of sulphide on the platinum electrode (although the present sediments are not sufficiently sulphur-rich to cause problems) and the essential requirement of careful insertion of the electrodes so as to avoid entrainment of oxygen or other gases.

The major problems are, however, inherent in the natural system. The redox couples present will not be in equilibrium and may well not attain such at the electrode. Further, a rapidly reversible couple, if occuring at the electrode will generate a potential that may be little related to the overall potential within the system[75]. In general the electrode responds satisfactorily to only a few processes and does not respond to O_2/H_2O, SO_4^{2+}/H_2S, CO_2/CH_4, NO_3^-/N_2, and N_2/NH_4^+ or any reaction in the solid phase[77]. Of relevance to this study is that, in strongly reducing systems the electrode is sensitive to many of the minor species present, in particular, iron and arsenic

species, and as long as these are in steady state, if not equilibrium, then the redox potential may be of value[77]. Lindberg & Runnells[78] have related Eh measurement in ground water to Nernstian behaviour and found that the measurement of Eh was very misleading. Approximation to equilibrium is not possible in a natural system where active biotic processes are at work (Morris & Stumm[79]).

Several workers have used Eh as an "operational" parameter as suggested by Whitfield[75] and a good example was the work of Pearson & Stanley[80] on the assessment of the organic pollution of marine sediments. This "operational" use has been investigated and sanctioned by the Commission of the European Communities[81].

In view of the potential problems outlined above, Eh values measured during this study have been signalled, Eh^*, to distinguish them from theoretically described potentials.

5.3.2. EXPERIMENTAL PROCEDURE.

Eh^* measurements were performed on undisturbed grab samples taken during February 1982 and March 1983. Results were available down to 60 mm in each case. Additionally a core profile down to 370 mm was obtained during April 1985 when a significant change in sediment characteristics became apparent.

Determination was performed using a Radiometer specific ion meter PHM53 measuring over a range of +500 mV to -500 mV, and electrodes manufactured by Russell pH Ltd., Auchtermuchty, Fife. A calomel reference electrode (3.5 M KCl bridge solution) was used in conjunction with a platinum electrode fitted with a 3 mm long x 2 mm

diameter sensing plug. The platinum electrode was mounted on a Palmer stand which could be slowly wound into the sediment in discrete intervals with minimum disturbance. The electrode was accompanied by a probe consisting of a 2.5 mm diameter glass rod which proceeded just ahead to protect it from stones and other debris in the sediment. The probe was made as narrow as possible to avoid sediment disturbance. Prior to use the platinum electrode was carefully cleaned with fine abrasive paper[75] and calibrated against ZoBell solution. ZoBell solution was produced by mixing 250 cm^3 each of 0.003 M potassium ferricyanide and 0.003 M potassium ferrocyanide in 0.1 M potassium chloride 2 hours before use. The electrodes and Zobell solution were equilibrated to the water temperature before being used. The sensing electrode had an operating length of 300 mm. The reference electrode was clamped in place so that the sensing plug was below the water surface but ensuring that the KCl solution level in the electrode was more than 30 mm above water surface (to prevent ingress of contaminants into the electrode).

After positioning the platinum electrode a reading was noted after 60 s. A second reading was observed at 120 s and if stable (drift <1 mV) this reading was recorded, otherwise the reading observed at 300 s was recorded. It was found that for readings below -100 mV stability was achieved within 30 s. The observed potential (E mV) at temperature (T ^{o}C) was converted to Eh^* (mV) relative to Standard Hydrogen Electrode by means of the formula

$$Eh^* = E + 244 - (T - 25)x0.76$$

as supplied by the electrode manufacturers.

5.3.3. RESULTS.

Table 5.9 tabulates the results obtained on each sampling occasion. The required modification for taking readings below an Eh^* value of -250 mV was not available during these surveys. However it is evident that important redox reactions occur below this potential at higher pH values. These include most significant C-N-S-H-O couples (Berner[22]) and $Fe^{2+}/Fe^{3+}/FeS/FeS_2$ processes (Drever[77]). However it is, in any case, probably pushing this "operational" parameter too far to involve a precise Eh^*, and it suffices to indicate that very low Eh values are involved.

date taken: FEBRUARY 1982

station:	7	12	14	16	21	35	39(i)	45
depth (mm)								
+5	+460	+465	+410	+450	+391	+465	+ 71	+460
surface	+455	+455	+407	+460	+387	+463	-108	+460
-10	+199	+219	+214	+194	+203	+231	-170	+222
-20	+ 35	+ 64	- 44	- 16	+ 8	+134	<-250	+139
-30	-205	-111	-131	-110	-137	- 41	<-250	- 55
-40	<-250	-237	<-250	<-250	<-250	-161	<-250	-202
-50	<-250	<-250	<-250	<-250	<-250	<-250	<-250	<-250
-60	<-250	<-250	<-250	<-250	<-250	<-250	<-250	<-250

date taken: MARCH 1983

station:	14	39(i)
depth (mm)		
+5	+405	+ 57
surface	+397	- 48
-10	+149	-221
-20	-141	<-250
-30	<-250	<-250
-40	<-250	<-250
-50	<-250	<-250
-60	<-250	<-250

date taken: APRIL 1985 at station: 39

depth	Eh*	depth	Eh*	depth	Eh*	depth	Eh*
+10	+390	-90	- 63	-190	-113	-290	- 90
surface	+392	-100	- 68	-200	-111	-300(r)	- 75
-10(a)	+145	-110(b)	- 81	-210	-112	-310	- 77
-20	+ 75	-120	- 84	-220	-110	-320	- 75
-30	+ 48	-130	- 92	-230	-108	-330	- 73
-40	+ 28	-140	-100	-240	-101	-340	- 76
-50	+ 12	-150	- 98	-250	-104	-350	- 70
-60	- 3	-160	-130	-260	-102	-360	- 68
-70	- 16	-170	-122	-270(c)	-100	-370	- 65
-80	- 46	-180	-124	-280	- 97		

TABLE 5.9. Measurement of Eh* (Eh observed) from 1982 to 1985. Depth in mm below mud-water interface, results in mV. Temperatures between 8.5-12°C. (a) 0-110mm very soft red mud, (b) 110-270mm silty, light brown mud, (c) 270-390mm dark, fibrous with plant debris. (i) Indistinct surface. (r) Reference electrode in mud for -300 to -370 mm.

5.4. ANALYSIS OF SEDIMENT CORE MATERIAL

5.4.1. CHEMICAL COMPOSITION.

Sediment material was subjected to analysis by several techniques. Bulk inorganic chemistry was determined by X-Ray Fluorescence Spectrometry as described in Chapter 9.2.1 and C, H, N was determined by elemental analyzer as described in Chapter 9.3. Major element chemistry was covered by Ca, Mg, Na, K, Si, Al, P, C, and N. Minor element determinands were chosen to indicate the existence of detrital material (Ti and Zr), aluminosilicates (Si, K, Mg, Fe, Rb), those affected by biogenic processes (Br, I, Mo) and trace metals which are readily surface-adsorbed. Three cores were chosen for analysis, these being station 14 (deepest point), 39 (near leachate entry) and 45 (near north inlet) as sampled in July 1983. Additionally a core from station 39 obtained in March 1983 was subjected to major element analysis for comparative purposes. This core was designated 39A. The results obtained are summarised in Table D.1. It will be noted that few data are available for the 0-3 cm segment of cores, as insufficient material was available after drying.

Table D.1 illustrates the concentration of elements found for each segment after adjustment for the composition of interstitial water. It has been assumed that the interstitial water has the composition of average loch water over the period 1981-1983. Since the only major effects will be for sodium and chloride this assumption may be reasonable. Unfortunately, the adjustment is exponential with respect to moisture content expressed as wet weight, and the results contain an ever increasing error as moisture content increases. The concentration of element i contained in the solid phase of the wet

sediment (X_{ia}) was calculated from the gross content of element i in the dried sediment (X_{it}) and that in the interstitial water (X_{iw}) by use of the formula:

$$X_{ia} = X_{it} - C(W/(100-W))X_{iw}$$

where C = 0.0001 for those elements expressed in %(w/w) and
1 for those elements expressed in mg kg^{-1}
W = % moisture (w/w, wet weight) in the sediment

For each segment the expression W/(100-W) was calculated and multiplied by the X_{iw} factors shown in Table 5.10. An indication is given of the correction required for higher levels of W. Only elements presenting corrections >1% are given.

element i	conc.* units	X_{iw}	W				
			75	80	85	90	95
Na	%	251.8	0.08	0.1	0.143	0.227	0.478
K	%	3.64	----	----	0.002	0.003	0.007
Cl	mg/kg	37.8	113	151.2	214.2	340.2	718.2
As	mg/kg	0.32	0.96	1.28	1.81	2.88	6.08
V	mg/kg	0.49	1.47	1.96	2.78	4.41	9.31
S	mg/kg	14.74	44.22	58.92	83.5	132.7	280.1

TABLE 5.10. Adjustment expression [$C(W/(100-W))X_{iw}$] for significant elements, i, at specified values of moisture content, W.
* refers to units of measurement in the sediment while X_{iw} values are in mg/l.

It is evident that such a general means of correction will not mirror the interstitial chemistry in the "native" sediment at the base of each core but it was not thought to be possible to grade correction increments down the core. From results presented in Chapter 5.5 it is likely that arsenic will carry the greatest error, being underestimated by up to 8% while at the same time silicon will be undercorrected.

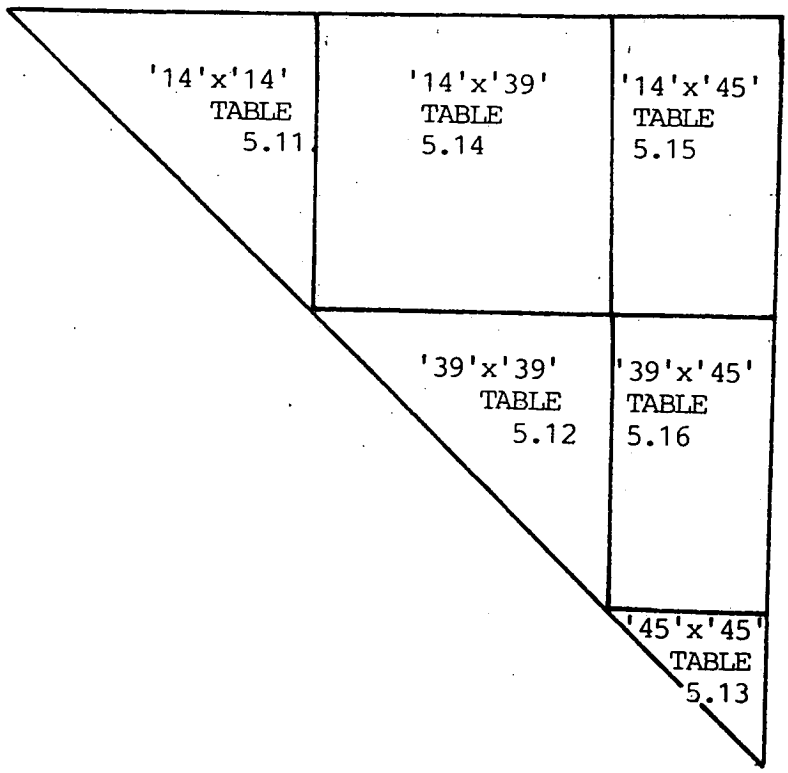
5.4.2. HORIZONS WITHIN A SEDIMENT CORE.

In order to gain an understanding of the inter-relation between segments within a core and also between cores a computer program "CLUSTER" (Appendix E.2) was written to provide a statistical comparison of segment chemistries. Comparison was achieved by cluster analysis of multivariate data (as given by Davis[19]) with two separate correlation systems, one by the use of correlation coefficient r_{ij} and the other using a distance coefficient d_{ij}. Both systems gave very similar results but as d_{ij} values are unbounded while r_{ij} are restricted to be between +1 and -1, a matrix of d_{ij} values was considered more easily discriminating. Standardised m-space Euclidian distances, d_{ij} were computed from

$$d_{ij} = \sqrt{\{\sum_{k=1}^{n}[(X_{ik}-X_{jk})/m_k]^2\}/n}$$

where X_{ik} and X_{jk} are the results obtained for the k^{th} determinand for segments i and j respectively and n is the number of determinands measured. So that the coefficient would not be biased by a numerically large set of results the equation incorporates a "standardization" procedure involving the division of all results for determinand k by m_k, a combined mean of results for determinand k over all the cores being compared.

The program created a single matrix containing all results (except for the incomplete data within the 0-30 mm interval) for cores from stations 14, 39, and 45 and each result standardised by the mean for that determinand. A second matrix was generated containing d_{ij} for comparison of each segment of the combined cores with all others. This produced a 45x45 element matrix with the following construction, each box indicating the cores being compared:



Tables 5.11 to 5.16 show the individual sections of this matrix. Note that segment 1 represents the 30-60 mm horizon and that 0-30mm is omitted. For each of these comparisons a dendogram was created. This involved pairing the segments with the lowest d_{ij} value (greatest similarity) and replacing the pair with a mean value of the two results for each determinand. d_{ij} was recalculated using this mean value in place of the separate ones and the procedure repeated until the last pair of grouped segments were combined (see Davis[19]). Dendograms were generated for relations within individual cores and these are illustrated in Figure 5.6. Distance coefficient analysis does not allow a degree of significance to be attached to the correlation[19] but in this instance such figures would be irrelevant. From Figure 5.6 it will be seen that for stations 14 and 39 the correlations compare well with the observed horizons (For key see Appendix C).

	segment number																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1																		
2	49																	
3	58	25																
4	81	54	30															
5	63	35	15	23														
6	73	47	25	16	14													
7	86	49	38	41	39	36												
8	95	62	52	55	55	51	24											
9	101	70	60	61	63	59	33	12										
10	106	78	68	68	71	66	44	25	16									
11	114	85	73	68	75	69	52	38	32	22								
12	120	92	80	76	83	77	60	47	41	31	14							
13	128	100	91	88	94	89	70	53	46	36	27	20						
14	127	98	89	88	93	88	68	57	50	40	28	19	26					
15	129	101	94	94	98	94	73	57	50	40	33	25	16	20				
16	130	103	96	96	100	97	76	61	53	43	37	30	21	24	8			
17	120	101	04	95	99	96	75	61	55	46	40	33	24	25	13	10		
18	122	91	85	87	90	87	64	53	48	41	38	33	32	26	22	21	17	

TABLE 5.11. Distance coefficients down core 14.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1																		
2	39																	
3	16	11																
4	15	16	15															
5	18	24	21	14														
6	21	30	28	24	20													
7	27	34	27	28	23	27												
8	29	40	36	32	25	29	19											
9	41	46	44	42	40	34	29	33										
10	82	86	87	85	84	71	79	81	55									
11	102	105	106	104	103	93	97	99	74	33								
12	96	98	100	99	99	88	92	95	70	37	21							
13	92	94	95	94	94	84	88	92	64	30	22	23						
14	92	96	98	97	99	90	94	98	71	43	37	36	18					
15	98	96	99	98	100	91	95	99	72	48	39	37	23	9				
16	91	89	92	91	94	86	90	95	69	52	54	48	36	25	25			
17	91	90	91	91	93	84	83	89	62	55	59	53	41	38	38	36		
18	89	89	89	90	91	83	81	89	62	60	66	59	49	46	46	42	12	

TABLE 5.12. Distance coefficients down core 39.

	1	2	3	4	5	6	7	8	9
1									
2	10								
3	14	10							
4	25	21	16						
5	31	28	23	9					
6	41	38	33	22	15				
7	67	64	60	47	40	35			
8	80	78	74	62	54	48	17		
9	77	74	70	60	53	42	31	25	

NOTE. Segment 1 represents the 30-60 mm horizon, and so segment 9 represents the 270-300 mm horizon, etc.

TABLE 5.13. Distance coefficients down core 45.

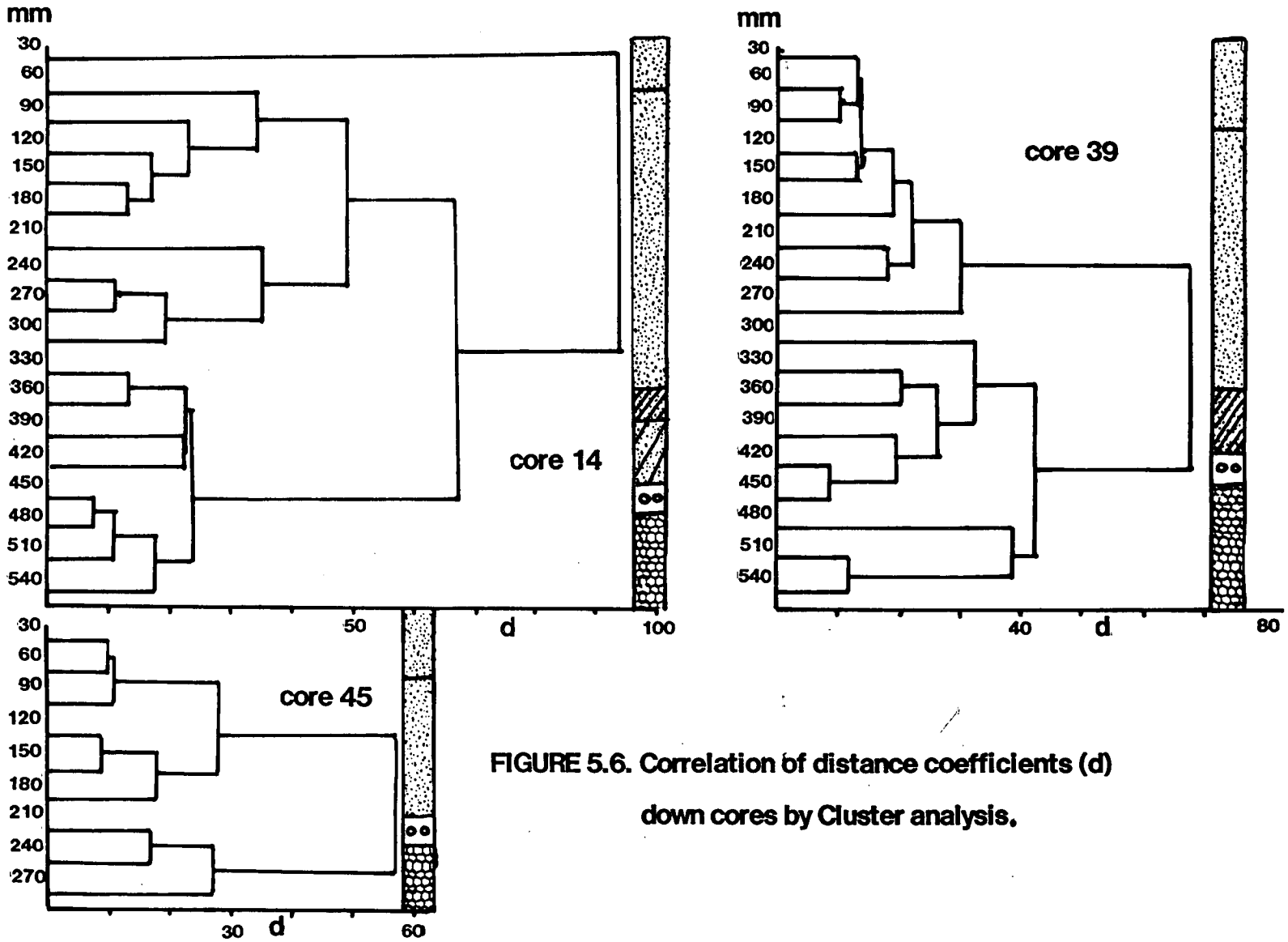


FIGURE 5.6. Correlation of distance coefficients (d) down cores by Cluster analysis.

For station 14 two separate sediment types are evident within the red-brown layer while the material in the grey layer is well correlated but of a type blending well with the "native" sediment below. The material above the grey layer is poorly correlated with that below but the extremely wet red layer at the surface is evidently very different from the whole of the rest of the core. Core 45 separates very nicely into the material of "native" sediment and that above. In this instance the upper, very soft, red layer is very similar to the red-brown layer below. Core 39 is more complex. The upper 270 mm are well correlated and so is the material of the grey and transitional zones. The latter zones are moderately well typed with the "natural" sediment but a definite difference exists between the material above and below 300 mm.

The break at which a real difference in chemical composition occurs relates to the transition to "native" sediment at station 45 only. At the two stations that regularly suffer anoxic conditions the break occurs immediately above the grey zone and it is likely that this zone represents the pyrite-formation horizon. Again, the upper 60 mm of core 14 will represent a very different redox regime compared to the centre part of the core and the definite break here may be a distinct indication of this change.

5.4.3. RELATIONSHIP BETWEEN CORES.

Every segment of material in cores 14, 39, and 45 were compared with every other segment in the other cores and the distance coefficients are tabulated in Tables 5.14 to 5.16. Figure 5.7 shows the best relationships between individual segments. If the best d value was >50 then it was omitted. Superimposed upon this are sediment type

	segment number																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	93	50	53	67	61	65	52	54	61	71	79	84	87	91	89	90	89	81
2	96	56	60	75	68	73	58	57	63	72	81	85	86	92	88	89	87	80
3	96	53	58	74	67	72	56	58	65	74	83	87	89	93	90	91	89	81
4	93	52	57	74	67	72	56	57	63	72	81	85	87	92	89	90	89	82
5	91	50	55	72	65	70	56	60	66	74	82	87	90	92	91	93	91	83
6	95	54	52	63	61	65	54	56	61	68	73	78	82	85	84	85	84	77
7	90	43	48	65	58	63	47	56	62	70	76	80	87	84	87	88	86	75
8	86	42	45	62	55	61	48	58	64	72	79	84	91	89	92	93	92	82
9	92	51	46	55	54	55	33	37	41	47	51	55	63	60	63	65	63	53
10	118	90	75	65	77	71	64	58	54	49	35	32	41	42	47	50	49	50
11	134	109	97	91	100	95	85	79	74	67	52	42	48	41	49	52	49	54
12	132	105	94	90	97	93	83	75	72	65	55	45	48	44	48	50	45	49
13	128	101	91	88	94	90	77	67	62	54	41	32	35	30	33	34	31	36
14	132	107	99	98	103	99	84	71	64	54	45	35	30	31	25	25	23	33
15	133	108	101	102	106	103	86	73	67	57	49	39	33	32	26	25	22	33
16	129	104	97	99	103	100	83	69	64	54	51	44	36	42	32	29	28	34
17	126	98	92	94	97	95	77	69	64	56	51	47	48	41	39	35	34	29
18	126	97	92	95	97	95	78	70	66	60	56	53	54	48	46	42	40	33

TABLE 5.14. Distance coefficient correlation between segments of core 14 (across page) and core 39 (down page).

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	95	52	53	65	60	62	37	43	49	56	63	68	75	71	74	75	74	62
2	97	55	55	66	62	64	37	42	47	54	61	65	72	69	71	72	72	59
3	99	59	57	67	64	64	37	39	44	50	57	62	69	65	67	69	68	56
4	103	65	61	69	67	67	38	32	34	38	47	52	57	56	55	57	57	46
5	104	68	63	70	69	68	39	29	29	32	40	45	50	50	49	50	52	42
6	109	75	69	74	75	73	45	36	32	30	33	37	45	39	41	43	45	35
7	121	94	87	89	92	89	66	48	40	31	32	31	22	35	22	25	31	35
8	131	106	99	99	104	100	79	61	52	43	39	35	23	34	21	23	29	39
9	130	104	96	96	101	97	75	63	55	46	37	33	33	24	24	25	30	34

TABLE 5.15. Distance coefficient correlation between segments of core 14 (across page) and core 45 (down page).

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	42	45	42	45	45	46	32	40	31	75	92	88	81	85	85	82	74	74
2	45	48	45	47	47	47	35	43	31	73	90	86	79	82	83	79	72	71
3	49	52	49	51	52	51	40	46	31	70	87	84	76	79	80	76	68	69
4	52	53	52	53	55	53	47	53	33	63	81	77	67	68	70	65	60	61
5	56	56	56	57	59	55	51	58	34	59	77	74	62	63	65	61	56	58
6	67	68	68	68	69	64	60	66	39	55	70	69	56	56	58	56	48	51
7	80	78	81	80	83	76	81	86	59	52	62	62	48	41	43	41	49	54
8	93	91	94	92	95	88	93	98	70	55	59	60	46	38	38	42	53	58
9	96	96	96	95	96	88	90	96	66	53	53	57	43	40	40	47	45	51

TABLE 5.16. Distance coefficient correlation between segments of core 39 (across page) and core 45 (down page).

NOTE. Segment 1 represents the 30-60 mm horizon, and so segment 9 represents the 270-300 mm horizon, etc.

(coded as shown in Appendix C) and horizon boundaries taken from Figure 5.6. These three parameter sets were used to identify segments within the cores that were well correlated and did not cross any sediment type or physical boundaries. Two such "segment sets" were indentified and these are indicated in Figure 5.8. Set '2' was extended to create sets '3' and '4' by allowing well correlated segments to trangress physical boundaries. It will be evident from the figures that the upper parts of cores 14 and 39 do not form a set and are not related to any segment of core 45 except for 30-60 mm segment, where the correlation is not good. "Segment sets" so formed were considered to represent inter-related sediments that could be investigated for chemical relationships.

5.4.4. RELATIONSHIP OF ELEMENTS WITHIN HORIZONS

Each segment set was investigated to ascertain which, if any, of the elements were spacially correlated. A t-test was initially applied to the individual elements within sets 1 and 2 in order to determine if any element was equally abundant within the sets. This was achieved by comparison of the means, using a standard deviation of 5% in all cases (this approximation was used after consulting Table 9.4). No significant difference was found for the abundance of aluminium in either set. All other elements were differently abundant. On applying a F-test to the standard deviation about the mean for aluminium it was found that it was not significantly greater than 5% in either set 1 or 2. All other elements showed considerable variation in concentration within each set. Elements investigated were the "key" elements (as defined below), Ca, Si, organic C, Ti, Al, and Fe.

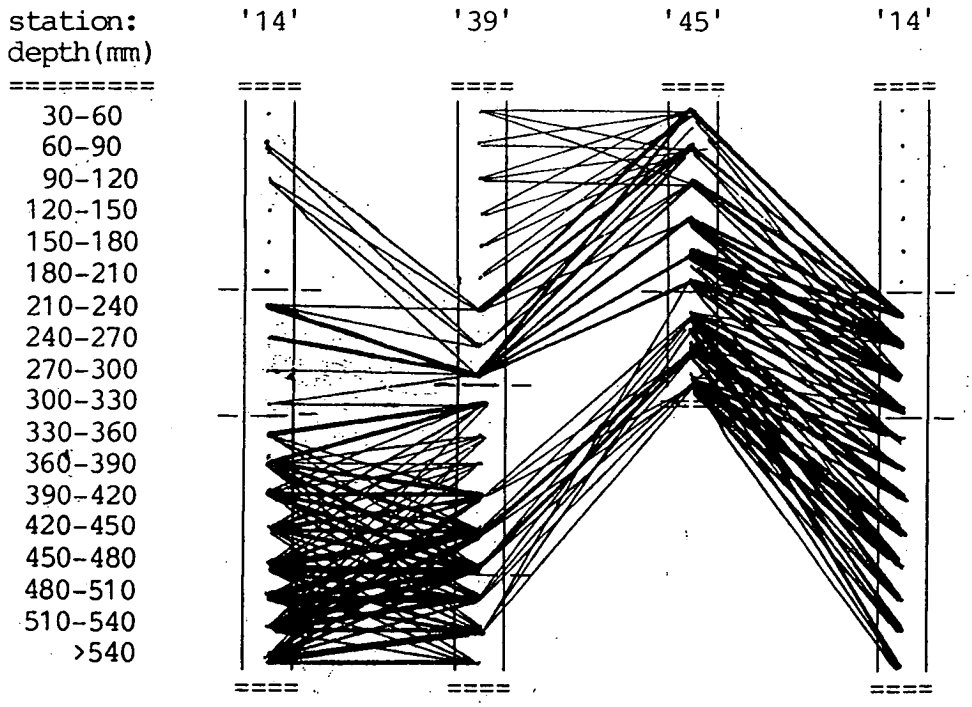


FIGURE 5.7. Good correlations between inter-segment d values incorporating dendogram boundaries. ——— represents 50>d>40, ——— represents 40>d>30 and ▬▬ 30>d. Physical boundaries are shaded as in Appendix C.

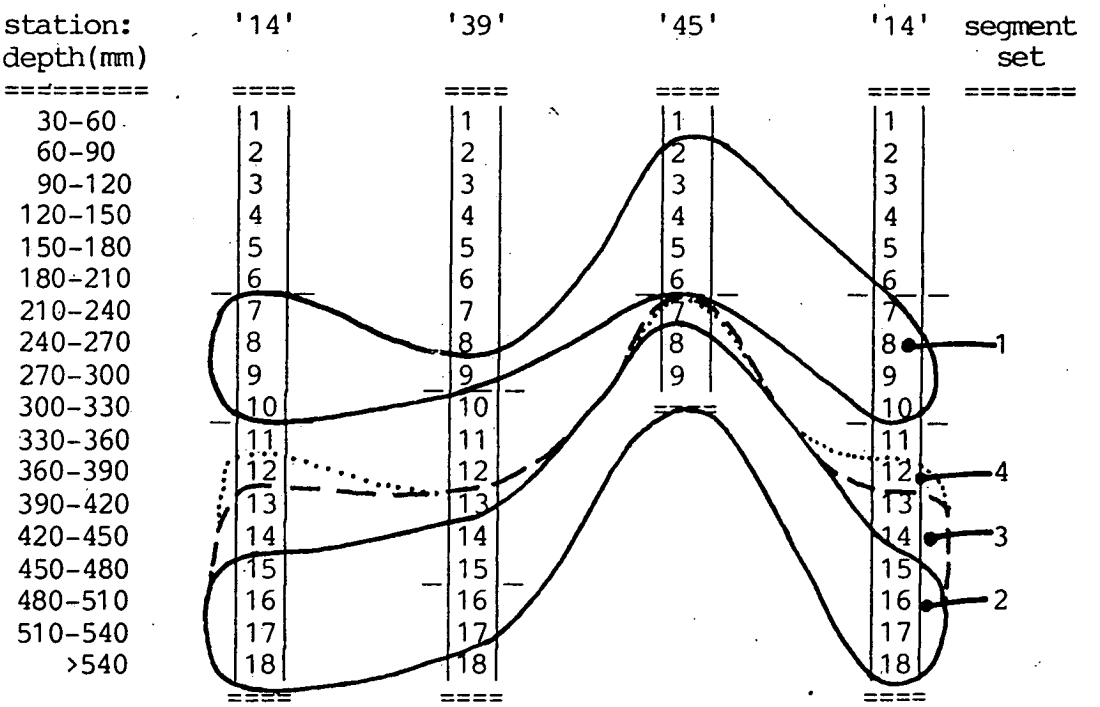


FIGURE 5.8. Segment sets formed by d values between segments and bounded within dendogram groups. Sets 1 and 2 are also bounded by physical type.

The similar abundance of aluminium in each set must be coincidental but the lack of variability of concentration within each set indicates that aluminium is either insensitive in its reactions occuring within the loch water and sediments or else that it is effectively physically redistributed so as to eventually achieve even distribution.

Pairs of elements were chosen for comparison by the generation of a Pearson's correlation coefficient for segments within a set. Elements that are known to undergo similar diagenetic processes were grouped and of these one abundant element was used as a "key" element against which to correlate the others. The groups will be discussed in Chapter 5.7 and Table 5.17 lists the pairs tested and numerates those found to be significant ($r>.95$ or $r<-.95$). Correlation was tested between all pairs of "key" elements. The following significant correlations were found Fe-Ti (r=0.999 & 0.994), Fe-Si (r=0.998 & 0.986), Ti-Si (r=0.996 & 0.995), and Fe-Al (r=ns & 0.984) where the figures in parenthesis represent set 1 and set 2 respectively. No others were significant.

An individual concentration within a segment cannot be considered to be truly independent of the result for that element found in adjoining segments and therefore the correlation coefficients found need to be interpreted with care. Groups of elements, affected by similar diagenetic processes are discussed in Chapter 5.7. In order to broaden discussion during Chapter 5.7, Chapter 5.5, on interstitial water, and 5.6, on radionuclide dating, are considered next.

elements:		set: 1	2	3	4
Ti	- Zr	.989	.998	--	.999
Ca	- Sr	.993	ns	--	--
	Ba	ns	ns	--	--
Al	- Si	ns	ns	--	--
	K	.981	--	--	.987
	Mg	.991	--	--	.991
	Fe	.984	ns	--	--
	Rb	ns	.978	--	--
Si	- K	.994	--	--	.997
	Mg	ns	.983	--	.975
	Fe	.998	--	--	.993
	Rb	.993	--	--	.995
Fe	- Mn	ns	ns	--	--
	Zn	ns	ns	--	--
	Cu	ns	.992	--	--
	S	ns	.975	--	--
	As	ns	ns	--	--
organic C	- S	ns	ns	--	--
	N	ns	.992	--	.987
	P	ns	--	--	.972
	I	ns	ns	--	--
	Br	ns	ns	--	--
	Cr	ns	ns	--	--
	Cu	.985	ns	--	--
	Ni	ns	ns	--	--
	Pb	ns	ns	--	--
	V	ns	ns	--	--
	Zn	ns	ns	--	--
	As	ns	ns	--	--

TABLE 5.17. Correlation between elements for each segment set (ns not significant, -- not tested).

5.5. INTERSTITIAL WATER CHEMISTRY

The accuracy of results presented in this section for the analysis of interstitial waters must be carefully considered in light of the reservations expressed in Chapter 5.2.2. It is considered that, although the absolute accuracy of the determinations may be flawed, oxidation-reduction relationships and concentrations relative to other segments of cores will have been maintained. It is not the intention of this section to provide a consideration of the results, but rather to provide data for further consideration in various sections of Chapter 5.7, when the solid matrix and interstitial

waters may be considered together.

Cores were obtained during July 1983 and analysed on thawing. Interstitial water was obtained as described in Chapter 5.2.2 and subsamples were preserved as indicated. Analysis was undertaken according to the methods described in Chapter 9.1.2. These results are presented in Table 5.18. In addition a core from Station 39 was taken during April 1985 and treated as in Chapter 5.2.2 for the extraction and analysis of interstitial water. Table 5.19 presents the results obtained.

(a)Station 12.

depth	pH	S^{--}	Ca	Fe	Al	As	SiO_2	SO_4	PO_4	NO_3
water	9.9		3.2	<0.05	1.8	0.19	1.53	41	0.1	0.2
0-30										
30-60	9.24	0.18	24.2	3.41	8.72	2.91	1.51	22	8.3	0.1
60-90	9.2	0.16	3.6	0.10	4.11	1.6	0.75	36	3.4	0.1
90-120	9.0	0.13	1.1	0.05	0.91	1.44	0.51	32	1.1	0.1
120-150	8.66	0.05	1.0	0.05	0.36	1.0	1.54	29	0.7	0.2
150-180	8.52	0.08	0.6	0.10	0.21	0.65	1.68	34	0.9	0.1
180-210	8.14	0.07	7.8	0.09	0.10	0.67	1.82	38	1.4	0.1
210-240	7.8	0.06	12.2	0.03	0.22	0.42	1.96	67	0.8	0.1
240-270	7.96	0.04	14.1	0.02	0.36	0.65	2.19	87	0.8	0.3
270-300	7.54	0.16	12.1	0.20	0.34	0.31	1.77	72	1.3	0.6
300-330	7.86	0.18	10.9	0.35	0.31	0.12	3.64	63	0.4	0.3
330-360	8.2	0.08	13.6	0.37	0.14	0.06	7.28	60	0.5	0.3
360-390	7.77	0.06	14.1	0.26	0.2	0.06	9.89	56		
390-430	7.86	0.08	12.7	0.16	<0.1	0.02	11.2	58		

(b)Station 16.

depth	pH	S^{--}	Ca	Fe	Al	As	SiO_2	SO_4
0-30								
30-60	9.35	0.36	1.1	1.11	1.1	3.1	1.21	35
60-90	9.26	0.26	3.2	0.06	1.65	1.13	1.21	29
90-120	9.09	0.11	2.1	0.09	2.71	0.8	1.07	25
120-150	9.02	0.16	3.6	0.03	0.47	0.83	0.89	32
150-180	8.98	0.09	7.7	0.01	0.43	0.65	1.49	26
180-210	8.86	0.13	15.9	0.06	0.11	0.61	2.89	28
210-240	8.53	0.11	14.1	0.01	0.24	0.45	1.91	42
240-270	8.29	0.32	12.7	0.13	0.16	0.41	2.61	45
270-300	7.79	0.36	14.3	0.51	0.32	0.11	1.77	69
300-330	7.81	0.38	16.1	0.27	0.17	0.08	6.58	91
330-360	7.41	0.28	15.5	0.22	0.21	0.04	10.5	65
360-390	7.65	0.23	12.9	0.37	0.21	0.06	18.7	49
mm		mg/l	mg/l	mg/l	mg/l	mg/l	mg/l Si	mg/l S

mg/l P	mg/l N

(c)Station 35.

depth	pH	S^{--}	Ca	Fe	Al	As	SiO_2	SO_4
0-30								
30-60	9.36	0.18	2.14	0.62	6.44	1.31	0.75	72
60-90	9.38	0.15	87.1	5.11	16.1	1.17	0.65	87
90-120	9.27	0.15	3.1	0.99	2.75	0.8	0.79	61
120-150	9.14	0.17	1.2	0.12	1.11	1.23	0.88	40
150-180	9.1	0.24	0.8	0.10	0.86	0.64	3.64	45
180-210	9.08	0.36	1.7	0.04	0.84	0.66	2.52	31
210-240	8.34	0.21	14.7	0.05	0.31	0.42	4.01	32
240-270	8.0	0.26	13.5	0.05	0.27	0.47	4.39	39
270-300	7.93	0.21	12.9	0.05	0.27	0.53	6.63	71
300-330	7.79	0.24	17.1	0.01	0.16	0.02	7.98	162
330-360	7.91	0.18	13.2	0.06	0.24	0.05	13.2	82
360-390	8.1	0.11	14.9	0.04	0.27	0.08	11.5	65
mm		mg/l	mg/l	mg/l	mg/l	mg/l	mg/l Si	mg/l S

TABLE 5.18. (continued) Analysis of interstitial water for cores taken July 1983. All determinands are dissolved species defined in Chapter 9.

depth	pH	S^{--}	Ca	Fe	Al	As	SiO_2	SO_4	PO_4	NO_3
water	8.1	0.01	15.5	0.030	0.0105	0.036	4.11	62	0.04	6.3
int'face	8.1	0.03	13.8	0.029	0.0095	0.104	3.92	35	0.01	4.6
0-30	8.3	0.33	16.1	0.536	2.80	>1	1.82	35	0.01	0.3
30-60	8.8	0.62	8.0	0.138	1.35	0.36	1.12	29	0.18	0.2
60-90	8.9	0.20	8.6	0.096	0.91	0.63	1.35	29	0.16	0.3
90-120	9.1	0.14	6.0	0.285	1.56	0.71	1.12	60	0.03	0.2
120-150	9.1	0.47	4.8	0.066	0.345	1.06	1.21	41	0.01	0.1
150-180	9.0	0.30	6.3	0.196	0.23	0.75	1.68	82	0.01	<0.1
180-210	8.8	0.18	8.2	0.026	0.065	0.60	2.29	71	0.01	<0.1
210-240	8.4	0.14	15.5	0.132	0.24	0.40	4.15	178	0.01	<0.1
240-270	8.1	0.06	13.3	0.197	0.69	0.77	4.99	124	0.01	0.4
270-300	7.8	0.06	16.0	0.097	0.225	0.55	6.16	126	0.01	0.5
300-330	7.6	0.04	10.9	0.181	0.365	0.40	7.89	77	0.01	0.3
330-360	7.6	0.06	11.2	0.889	0.385	0.14	10.3	58	0.02	0.2
360-390	7.4	0.05	16.0	0.145	0.100	0.08	14.0	59	0.01	0.4
mm		mg/l	mg/l	mg/l	mg/l	mg/l	mg/l Si	mg/l S	mg/l P	mg/l N

TABLE 5.19. Analysis of interstitial water of core from station 39 taken April 1985. All determinands are dissolved species defined in Chapter 9.

5.6. DATING OF CORE PROFILES.

Material from the length of core 14 was subjected to ^{210}Pb and ^{137}Cs dating. I am very grateful to A.B.MacKenzie of the Scottish Universities Research and Reactor Centre, East Kilbride, Glasgow for carrying out this work on my behalf.

^{137}Cs was measured directly by γ-ray counting while ^{210}Pb was determined by α-counting of its daughter ^{210}Po. This procedure required dissolution in acid and, after spiking with ^{208}Po and removing iron by solvent extraction, the Po was electrodeposited onto copper foil. The ^{210}Po was measured by counting of α-emissions. Detailed procedures are contained in MacKenzie et al[82] and MacKenzie and Scott[83].

^{137}Cs ($T_{1/2}$ 30.23 years) in freshwater occured entirely as a result of nuclear weapons testing from 1960-1970 giving a series of depositional peaks, the most notable being around 1963. Although generally considered as a conservative element, a minor proportion becomes incorporated in the illite fraction of clays by ion exchange of potassium (A.B.MacKenzie, personal communication; and others, see Swan et al[84]) and this fraction is that of interest for the present study. The work carried out by S.U.R.R.C. failed to identify any peaks, due to the relatively low clay content, high sedimentation rate and degree of sediment turbation.

^{210}Pb, a member of the ^{238}U natural decay series has a half life of 22.26 years and occurs in water due to the atmospheric decay of short-lived ^{222}Rn, released from decay in rocks, via daughters to

^{210}Pb which is either "rained out" or dry-deposited. This contribution of ^{210}Pb is 'unsupported' by the parent. It is reported that most of the element is removed to the sediment at times of high phytoplanktonic activity[85] although, in Kinghorn Loch, with such a high authigenic input, it is likely that other processes also cause removal to the sediment. A significant, and other dominant[85], component also occurs that is produced *in situ* by the decay of radioactive parents in the sediment detrital minerals. This component is termed the 'supported' fraction. Most models used for evaluating dating results rely on compliance with four constraints[84] namely:

(1) a constant flux of unsupported ^{210}Pb

(2) a constant distribution of supported ^{210}Pb with depth in the sediment

(3) no post-depositional mobilization of ^{210}Pb or sediment within the sediment column

(4) a constant rate of sediment accumulation.

Deviation from these requirements are considered below.

(1) There is no reason to doubt this assumption, although regulation of input from Glassmount Reservoir will have generated a somewhat variable flow from the catchment.

(2) It is unlikely that the flux of ^{226}Ra contained in detrital minerals (or red mud solids, *etc*) will present a constant base to the dating for both "natural sediment" and the upper sediments but no means of evaluating the situation is available at this time. An assumption has been made that precipitating calcite will not contain any native ^{226}Ra and the correction used under (4) below, of assuming the concentration to be inversely proportional to calcium level, has been used.

(3) In very wet sediments considerable bioturbation and physical mixing occurs[84] while reductive recycling of hydrous iron oxides and digestion of organic matter must cause mobilization of ^{210}Pb within the column. Bioturbation will not have been a problem in this sediment but at least 70 mm are thoroughly physically mixed.

(4) The initial concentration of unsupported ^{210}Pb will be inversely proportional to calcium deposition, since calcium deposition is roughly proportional to the overall accumulation rate in the upper parts of the core (see Figure 4.10). Below this level the relationship does not hold but this is relatively unimportant since the level of cacium present is relatively stable and is likely to represent mainly shells and non-calcite calcium.

Figure 5.9 plots the levels of calcium found throughout core 14 relative to the (supported+unsupported) ^{210}Pb count data. Radioactive decay was expressed in terms of disintegrations per minute per g of sediment (dry weight), a "count" unit that has been abbreviated to d min^{-1} g^{-1}. Taking calcium as a measure of change in accumulation rate and dilution of ^{226}Ra, Figure 5.10 shows the ^{210}Pb count 'normalised' according to:

$$D_{ni} = D_{ri}C_i/C$$

where for segment i, D_{ni} = 'normalised' count rate, D_{ri} = measured count rate, C_i = calcium concentration, and C = mean calcium concentration for 420-560 mm depth.

Exponential decay curves have been fitted to the figure taking the 330 mm grey horizon (Appendix C) as representing the onset of significant pollution at an estimated date of 1962 (see Figure 4.4).

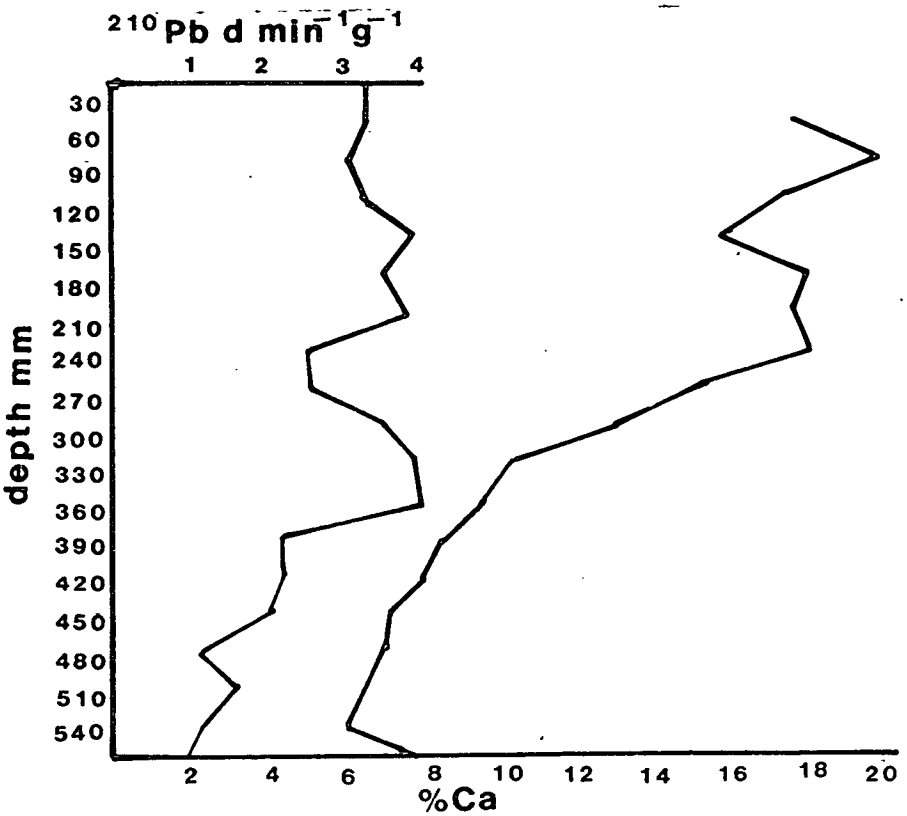


FIGURE 5.9. Decay of ^{210}Pb (supported+unsupported) and %Ca in core 14.

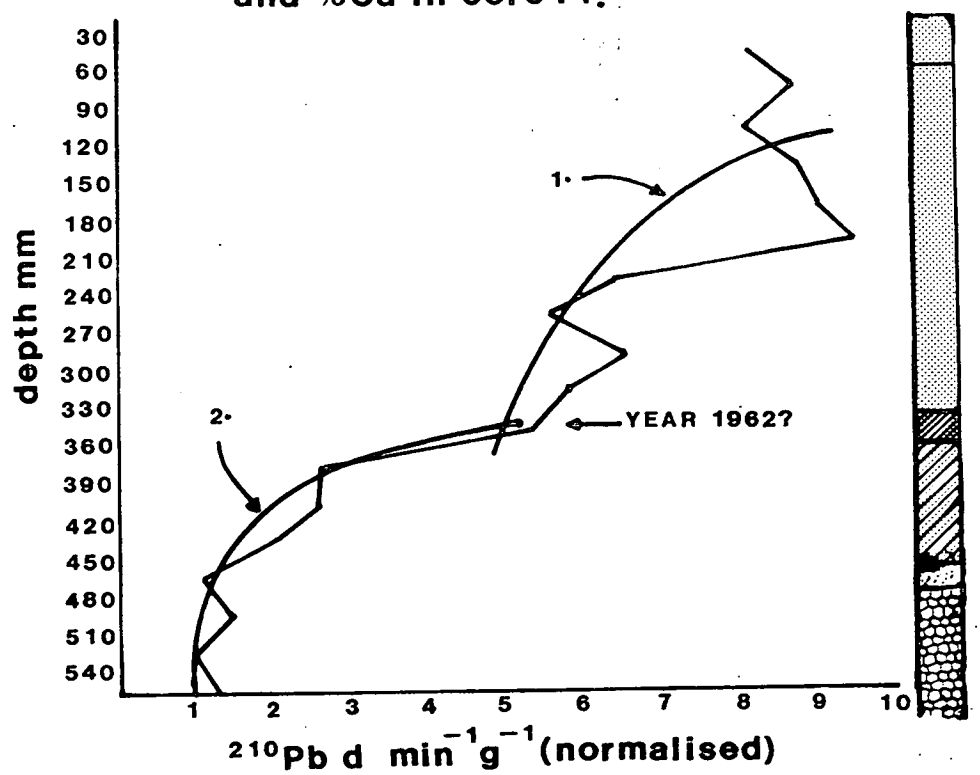


FIGURE 5.10. Decay of ^{210}Pb for core 14.

1· $T_{1/2}$ assuming 1962 horizon,

2· natural sedimentation rate 1.5 mm yr^{-1}.

Curve (2) was calculated by linear regression analysis on the data at S.U.R.R.C. and for a supported level of approximately 8 d min^{-1} g^{-1} represented a deposition rate for the "natural" sediment of 1.5 mm yr^{-1} (A.B.MacKenzie, personal communication). Curve (1) has assumed a similar supported level normalised to a "natural" deposition rate and has been drawn so as to comply with $T_{1/2}$ 22.26 years to a point at 330 mm taken to represent 1962 and assuming the upper 200 mm to be subject to total physical mixing. The representation in Figure 5.10 supports a mean sedimentation rate for 1962-1983 of 15.7 mm yr^{-1} and 1.5 mm yr^{-1} for pre-1962. Figure 5.10 provides further circumstantial evidence for considering the top of the grey layer as being the onset of significant pollution and must date it at approximately 1962. Thus taking 21 years of deposition as being represented by 360 mm of sediment and taking the accumulated deposition from Figure 4.10 combined with the moisture content of core 14 segments contained in Appendix C it is possible to assemble Figure 5.11 showing the mm of accumulated sediment over this time period. Initially it was assumed that the moisture contents were similar whereby annual accumulation was calculated according to

$$D_i = A_i D_t / A_t$$

where D_i = depth accumulated in year i (i= 1962 to 1983), D_t = total depth both in mm, A_i = annual accumulation for year i and A_t = total accumulation for 1962-1983, both in g m^{-2} yr^{-1}.

Since it was known that the upper 60 mm contained 92% moisture wheras the remainder of the upper core contained 87% moisture it was necessary to apply an iterative technique to bias the upper 60 mm in order to minimise error. The upper 210 mm were then averaged to

indicate the degree of physical disturbance and these results are shown in Figure 5.11. This treatment indicates a deposition in 1962 of 5 mm of the sediment column (as now is) as against an average pre-1962 rate of 1.5 mm. This suggests that the 1962 rate is over-estimated and therefore that the "oligotrophic" level of organic productivity shown in Figure 4.10 is erroneously high, a deposition rate of 100 g m^{-2} yr^{-1} being more appropriate than 250 g m^{-2} yr^{-1}. It may be recollected that the original estimate was obtained using a mean for productivity in oligotrophic lakes and the rate of degradation shown in Kinghorn Loch. It is evident that the phyto-plankton debris will have been more completely decomposed than in later years due to the higher oxidation regime present under oligo-trophic conditions, and therefore a lower flux to the sediment would be expected.

5.7. MINERAL FORMATION AND ORGANIC DIAGENESIS

5.7.1. DETRITAL ELEMENTS.

Titanium and zirconium are generally considered to originate entirely from solid detrital input and to be essentially unaffected by all subsequent chemical and biological processes. There is only a minor natural detrital input to the loch by way of the north inlet water and the dominant source of titanium will be from red mud solids swept past the settlement pond. From Table 2.7 it will be observed that red mud contains 4.9% TiO_2. This is enriched relative to natural detritus. Goldberg and Arrhenius[86] found that "very high" natural levels (>1.15% TiO_2) were almost always associated with basaltic debris. Table 3.1 displays the typical analysis of local basalt bedrock giving 2.5% TiO_2. Even if this material should completely weather to impure silica the titanium content would not be greater

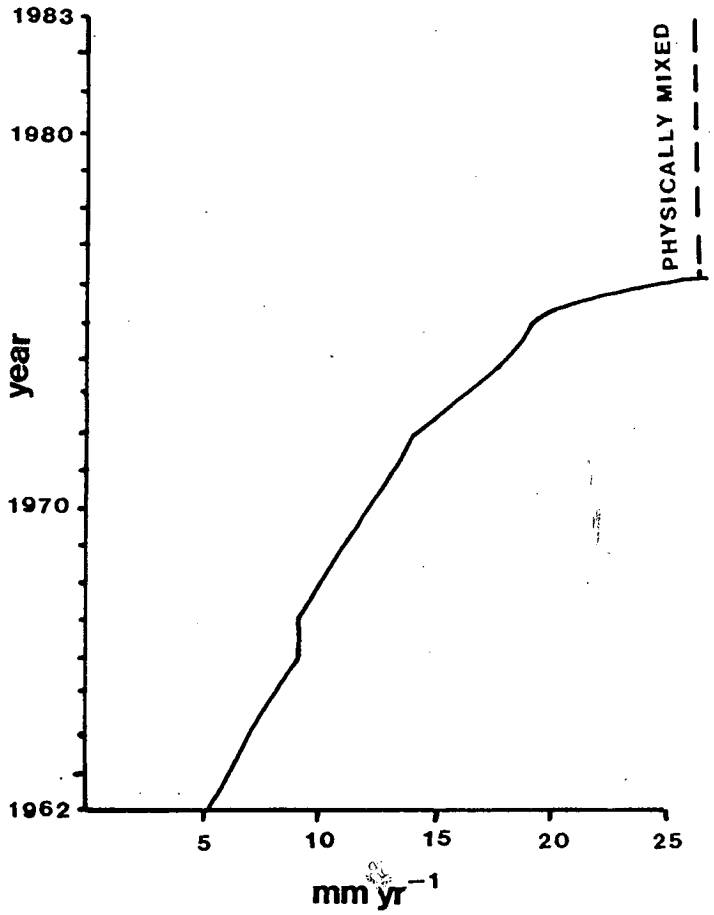


FIGURE 5.11. Projected deposition in mm yr^{-1} added to the sediment since 1962

than in red mud. Red mud was found to contain an Fe:Ti ratio of 7.9:1 while for local basalt it was 4.8:1. The lower material from core 14 showed a titanium content of 1.17% as TiO_2 and an Fe:Ti ratio of 7.7:1. This material accumulated over a very long time span with a slow detrital input. The material is rich in organic debris and this will have supplied additional iron to the loch. The titanium level is consistent with a basalt source. In the upper part of core 14 the ratio Fe:Ti was found to be 10:1 and both elements are thought to originate almost entirely from red mud. The concentration of Ti present in the upper parts of cores 14 and 45 would indicate a mineral detritus:precipitated material ratio of approximately 1:50 in the most recent sediment and approximately 1:10 in the oldest segments of the red-brown layer. It was observed in the previous section that iron is well correlated with titanium and provides further evidence for its detrital origin.

Chapter 2 suggests that the source of titanium will be ilmenite ($FeO.TiO_2$) intimately intergrown with the abundant hematite. The red mud flushed from the tip will be the finest particle sizes and will be in close association with detrital clays, probably originally of a sodalite type (Chapter 2). Iron is often transported on clay mineral[28], particularly at such a high pH. The association is likely to be stable with both Fe and Ti able to replace Al in the lattice[87] in addition to exchangable sodium.

However it has been shown (Chapter 5.5) that iron is greatly affected by the diagenetic environment and reaches high concentrations in the interstitial water. This high degree of correlation does however indicate that only a small fraction of the iron present is affected.

The fate of iron will be discussed later.

Zirconium is very well correlated in the lower set of the cores but to a lesser extent in the upper set. The ratio of Ti:Zr is not particularly variable. Due to an operational problem, the concentration of trace elements in the red mud, analysed by a pressed powder procedure, was not found and the ratio of Ti:Zr in red mud is not known.

It will be observed from the previous section that Ti is also well correlated with Si in both the upper and lower parts of the cores. In the lower part silicon levels are high, being 15-22% as Si, and are thought to have originated mainly from detrital sources. The detrital silica and clay minerals will have originated from basalt weathering and are therefore likely to be correlated with titanium. However in the upper parts of the cores silicon originated from dissolved contributions from the leachate and north inlet water, although approximately 20% of the total was provided by red mud solids. Silicon levels are variable within this set giving the range of 7.2-13.9%. The correlation within the set of segments is part of a Ti:Si correlation that exists throughout the upper part of the cores. However it is believed that the correlation is caused by a near-exponential change in concentration for distinctly different reasons. The decline in titanium occurs because of the ever greater quantity of calcium carbonate being formed while the detrital input remained nearly constant. The hypothesis governing the decline in silicon is part of a wider model and is put in Chapter 5.7.3.2.

5.7.2. CARBONATE MINERAL ELEMENTS

Magnesium does not show any correlation with calcium throughout the upper red and red-brown layers of the cores. This reinforces the findings of Chapter 4.7.1 which concluded that dolomite or magnesium rich calcite were not formed in the loch and that most of the magnesium was associated with clay mineralogy. It is however probable that a small proportion of the magnesium present was held in calcite by solid solution.

Calcite forms solid solutions with various cations including Mg, Mn, Fe, and Sr. It will be noted from Table 5.17 that for segment set 1, Ca and Sr are closely correlated whereas Ca and Ba are not. Barium was not determined for the aqueous inputs to the loch, but for the formation of barite a level of approximately 1 mg l^{-1} would be required. This is unlikely to have been reached. However the occurance of microenvironments, either by release of sulphate during sulphide oxidation or within micro-organisms could yield sufficient sulphate to cause deposition of barium sulphate. Figure 5.12 plots the relationship between barium and total sulphur in the upper parts of cores 14, 39, and 45. Some general correlation is evident although it is not linear. By forward reference to Chapter 5.7.5.1. It will be noted that most of the solid phase sulphur in the sediment is organic. Thus it is possible that any barium may be associated with organic sulphur rather than sulphate. However Ba is not correlated with organic (or inorganic) carbon. It has been reported by Taylor[88] that Ba^{++} may substitute for K^{+} in clays due to their similar ionic radii (1.34 Å Ba^{++} and 1.33 Å K^{+}). However whereas Al is resonably well correlated with K, Figure 5.13 indicates that no such correlation exists, in the upper parts of the cores, with Ba.

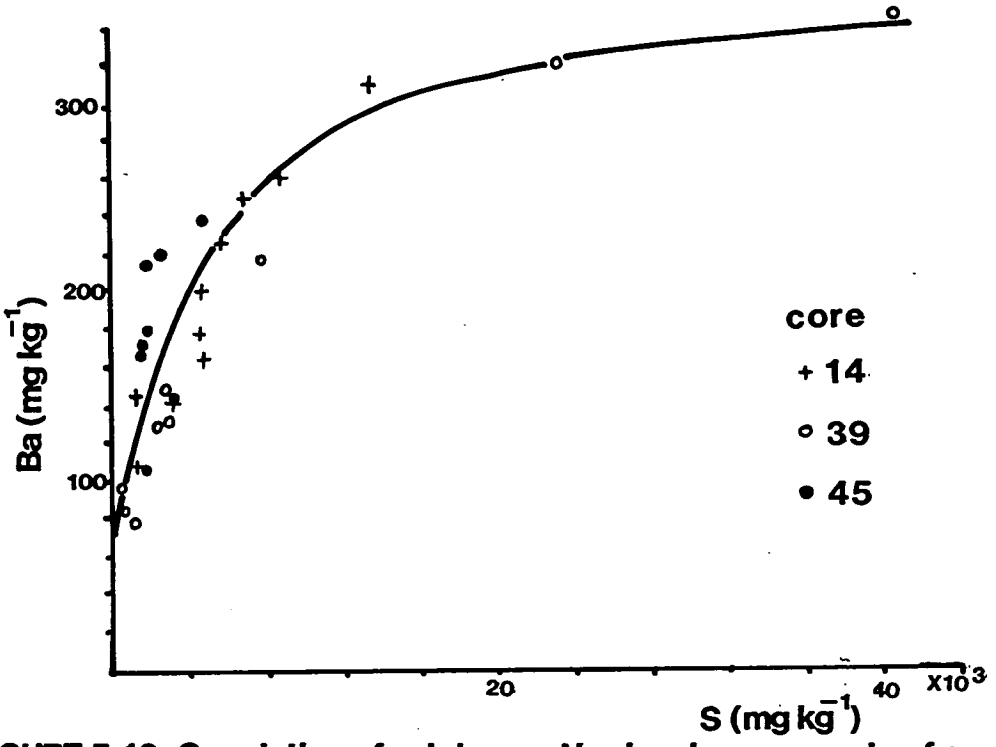


FIGURE 5.12. Correlation of sulphur and barium in upper parts of cores

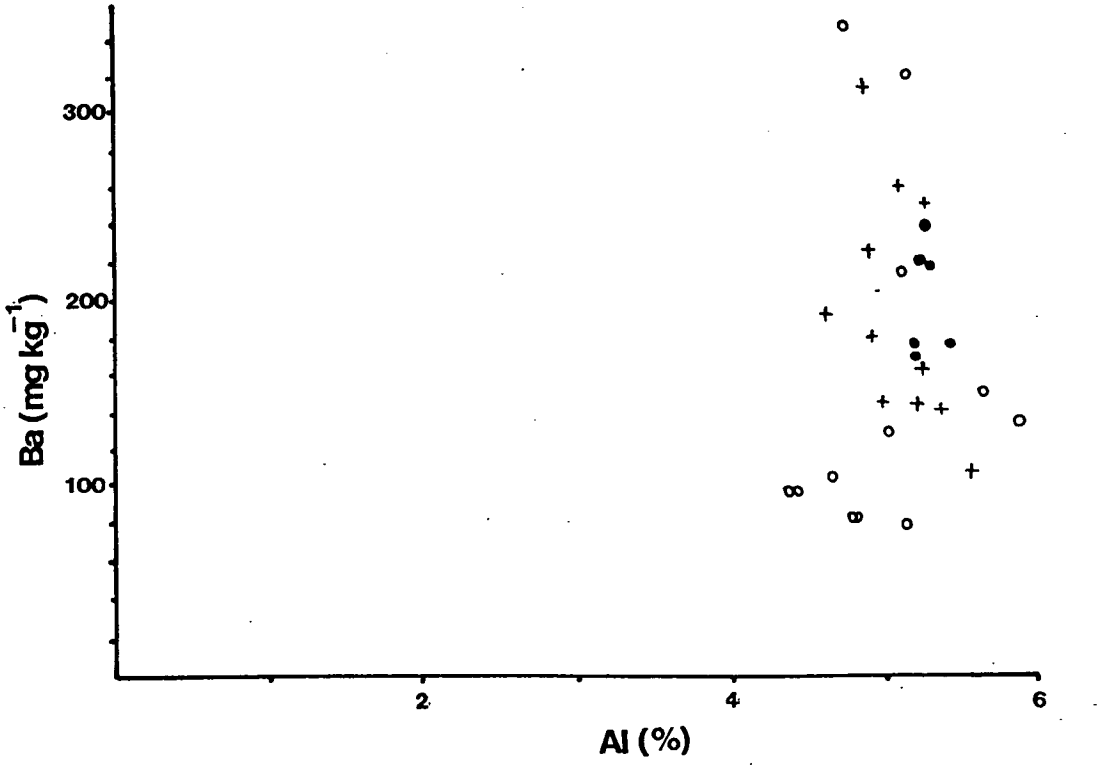


FIGURE 5.13. Correlation of aluminium and barium in upper parts of cores

Thus no definite sink for Ba has been identified, although it is likely to be associated with sulphur in organic matter.

Strontium forms solid solutions with calcite and to a greater extent with aragonite and dolomite. Turekian and Wedepohl[89] determined the ratio of Ca/Sr in oceanic clays and calcites and Shimmield[26] also correlated Sr and Ca in this way for oceanic deposits. Clays were enriched with Sr relative to calcites and a positive Sr intercept occured (at approximately 300 mg kg^{-1}) for clays but not with calcites. Figure 5.14 plots the relationship in the upper parts of the cores from Kinghorn Loch and excellent correlation was found with an intercept at the origin. Thus Sr is evidently associated with calcite giving a formula of $Ca_{0.996}Sr_{0.004}CO_3$. This is lower than the 0.006-0.015 Sr contribution found in oceanic calcites[26].

The relationship between calcium and inorganic carbon is investigated in Figure 5.15 and this shows a slight deviation from stoichiometric calcite at low Ca levels such that a positive Ca intercept occurs at 2% Ca. This would indicate that, for very low levels of calcium only, Ca at 2% of the sediment is associated with clays. Due to bunching of the points at higher concentrations this may not, in fact, be a real effect.

As has been indicated previously calcite is rarely pure and various impurities occur. Due to the high biological productivity of the water it is possible that biogenic apatite may form. Thus some of this calcium "excess" may be associated with apatite. This control of eutrophication by sedimentation, including calcite formation, was covered in Chapter 4.7.5. Additionally calcite may absorb sulphate

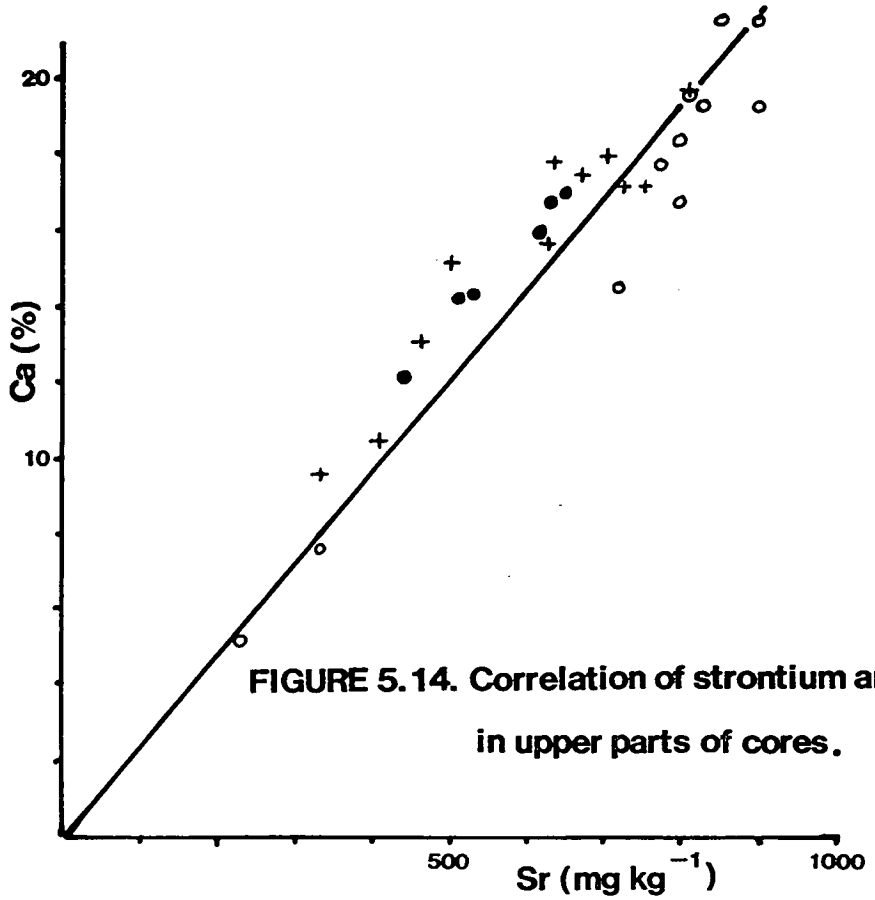


FIGURE 5.14. Correlation of strontium and calcium in upper parts of cores.

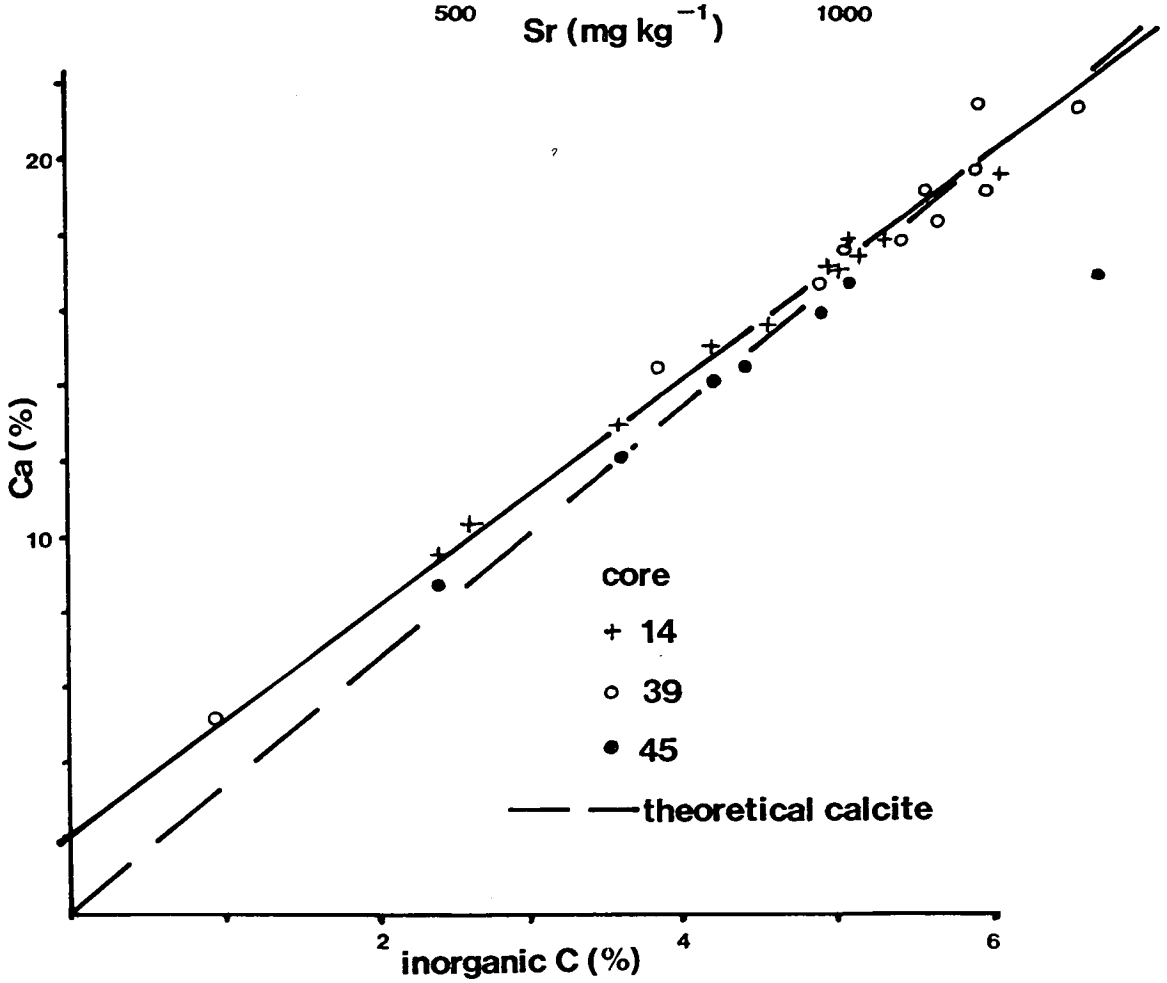


FIGURE 5.15. Correlation of inorganic carbon and calcium in upper parts of cores.

and alkali metals. These ions are particularly liable to be absorbed at rapid calcite growth rates, as occurs in Kinghorn Loch. Absorption of sulphate and sodium is linearly related to the rate of growth (Busenberg and Plummer[90]). For a sodium content of 10^{-2} M it was found that biogenic calcites could contain up to 0.1% Na. Sulphate provided 0.2-2.6 mol % of anions with a mean for calcite of less than 1%. Sulphate was found to significantly reduce the rate of crystal growth. Ishikawa and Ichikuni[91] reported similar results for the levels of sodium in calcite and suggested that Na and K filled interstitial sites in the lattice.

Additionally it was found that hydroxide was present in magnesium calcites and related to Mg content. Negligible hydroxide was present in pure calcite[91]. The hydroxide is probably present as co-precipitated magnesium hydroxide. In the most recent sediments of Kinghorn Loch it will be seen (Chapter 5.7.3.2) that magnesium is substantially enriched relative to Si and Al. At pH 10.3 the loch would be supersaturated with magnesium hydroxide (as brucite) and the pH may force the co-precipitation of magnesium and hydroxide into the calcite lattice rather than generate brucite as a separate phase or as a mixed layer clay mineral.

Samples of loch sediments were taken from cores 12, 14, 16, and 35 at 60-90 mm depth and at depths representing "natural" sediments and also an intermediate position. The samples were submitted to the Department of Applied Geology at the University of Strathclyde for X-ray diffraction studies. All the samples were found to contain calcite and quartz. Calcite diminished with segment depth while quartz increased. No other non-clay mineral phases were observed.

Analysis of the clay components will be considered in Chapter 5.7.3.3.

5.7.3. CLAY MINERAL FORMATION

It will be observed from Table 5.17 that aluminium and silicon, the primary clay forming elements are not well correlated in any part of the cores. It is known from X-ray diffraction studies (Chapter 5.7.2.) that detrital quartz is present in significant quantity in the "natural" lower parts of the cores, but only to a very minor extent in the upper parts. It is to be expected that correlation should be poor in the "natural" sediment. However, upper-core material was generated almost entirely from soluble species and a correlation would be expected if aluminosilicates were formed.

Silicon is poorly correlated with organic carbon in both the loch water and the sediment. References to Chapter 7 indicate that diatom populations were absent in the loch and that phytoplanktonic assimilation of silicon would be insignificant. Other processes involving silicon including clay mineral formation are considered to be abiogenic and are insignificant in most lakes[21], although not in Kinghorn Loch.

Silicon was found to be well correlated with potassium for segment set 1. However, a wider consideration of the whole of the red and red-brown horizons yields a more complex picture. This is illustrated in Figure 5.16. Rubidium is similarly correlated and these results are shown in Figure 5.17. Rubidium and potassium have similar ionic radii (1.48 Å and 1.33 Å respectively) and would be expected to be interchangeable in the lattice. The figures support

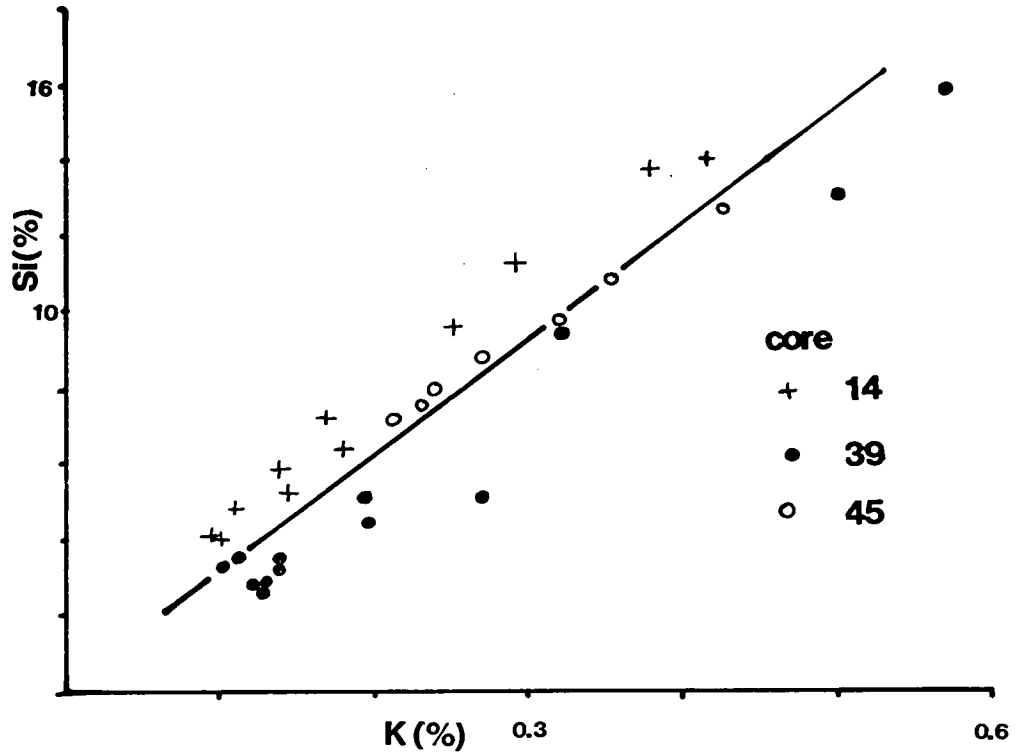


FIGURE 5.16. Correlation of potassium and silicon in upper parts of cores.

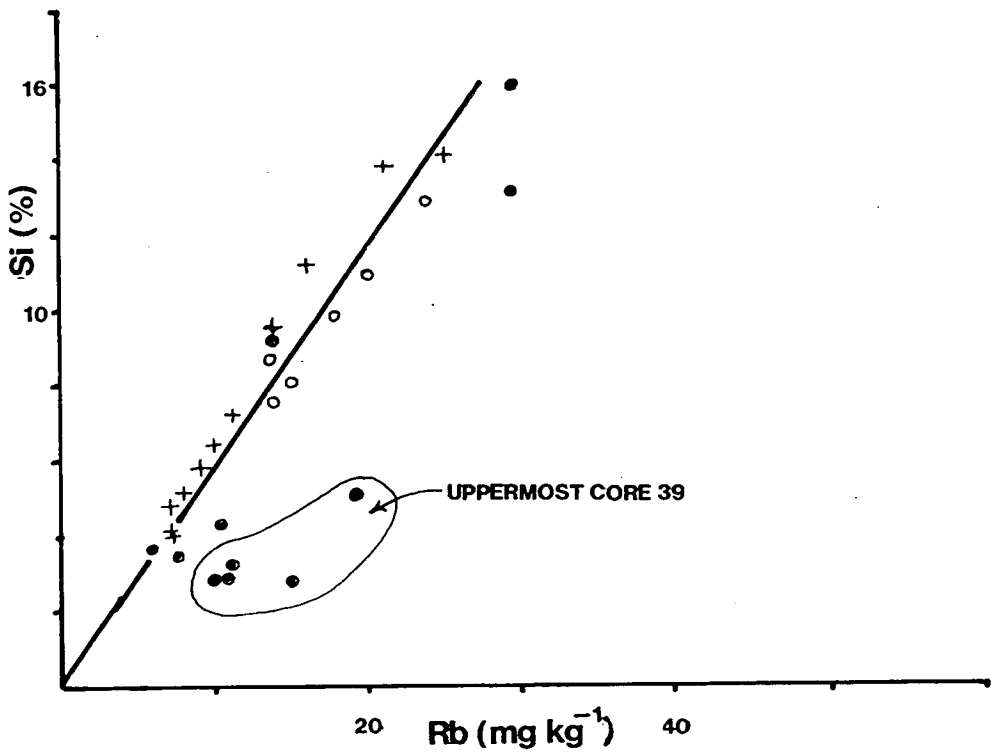


FIGURE 5.17. Correlation of rubidium and silicon in upper parts of cores.

this. Both elements are well correlated for cores 14 and 45 with a zero intercept. This indicates that all of the silicon is incorporated in clay minerals. However at lower levels of silicon in core 39 both elements are found to be enriched in the sediments. Magnesium is a major component of the clays (Chapter 5.7.3.2) but is in reduced supply near station 39, while alkali metals, brought in by the leachate, are at their greatest relative abundance at this station. Thus, away from station 39, K and Rb will be exchanged out of the sedimenting clays by the higher level of magnesium in the body of the loch. Figure 5.17 may show separate correlation line slopes for stations 14 and 45 and this is likely to indicate a slight difference in environment for exchangable ions.

Drever[77] reported that trace metals are adsorbed onto the surface of clay minerals while Jenny et al[92] reported the formation of a basic clay anion complex with zinc at high pH. Shimmield[26] considered the passive role of zinc in redox processes whereby zinc is released from iron and manganese oxyhydroxides and scavenged by zeolite structures in the sediment clays. Thus, with the degree of reworking of the sediments that evidently occured (Chapter 5.6), zinc should become equilibrated with clay content. Zinc does not show any correlation with aluminium but Figure 5.18 shows the correlation between zinc and silicon in the upper parts of the cores. The zero intercept indicates that both are completely involved in clay structures with no residual. In contrast Figure 5.18 also shows the lack of correlation in the lower part of the cores.

This close correlation between zinc and silicon requires a clay mineral, or closely related suite of clay minerals, to be present

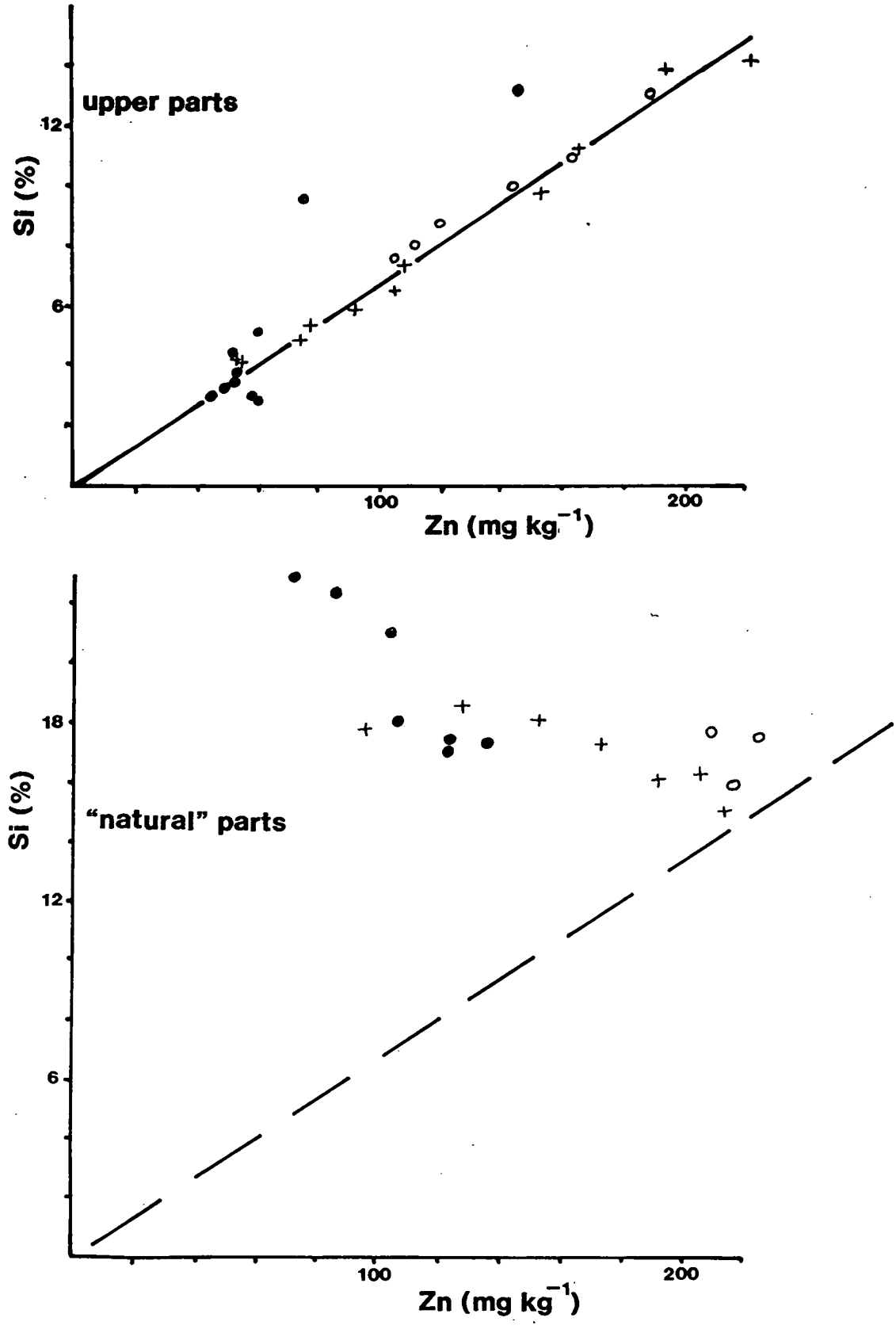


FIGURE 5.18. Correlation of zinc and silicon in cores

throughout the depth of the upper red and red-brown layers. These minerals must be present in minor amounts but proportional to the total clay content since the ratio of Al:Si in the upper parts limits the mineralogy of the dominant phases to those of low ionic exchange capacity. Chester et al[93], in studying the fate of trace metals in the smectite fraction of oceanic sediments found that sorption was controlled by a small zeolite component (clinoptillite).

The situation in Kinghorn Loch would require just such an efficient scavenger. The zeolite phillipsite ($K_{2.8}Na_{0.8}Al_{3.1}Si_{14.9}O_{36}.12H_2O$) is known to be formed (during diagenesis) in recent deposits and particularly in saline, high pH (>9) shallow basins[94,95]. It grows rapidly at or near the mud/water interface for Si concentrations below 5 mg l^{-1}. It is readily redissolved at depth[96] or at higher Si concentrations. Because of the rapid growth rate it incorporates iron oxyhydroxide and clay minerals, mainly smectites, in its structure. Phillipsite is formed from basaltic material in saline sediments and whether it could be synthesised in the loch is unknown. Sodalites also have a very high exchange capacity but, if brought in as red mud solids, would not be present in the required proportional abundance to silicon.

5.7.3.1. CORRELATIONS OF ELEMENTS IN INTERSTITIAL WATER.

It has been proposed by Berner[97] and Mackin and Aller[98] that interstitial water chemistry will reflect a local equilibrium with matrix minerals at each depth within a core. Mackenzie and Garrels[99] put forward a theory in 1966 that many detrital clay minerals should be readily dissolved and new minerals formed at normal temperatures within hours or days, if prevailing conditions of temperature,

pressure or chemical speciation were changed. This theory has been difficult to test under natural conditions since the authigenic component of sediments is far outweighed by detrital input. Mackin and Aller[100] set out to test the hypothesis by consideration of the relations between clay-forming ions in the interstitial water of nearshore sediments of the South China Sea. It was decided to undertake a similar examination of interstitial water chemistry for Kinghorn Loch sediments. Two distinct advantages exist. Any equilibrium within the interstitial water chemistry must be evidence of very recent authigenic clay mineral production. Also, existing clay minerals will be predominantly poorly crystallised (having been of recent origin), and the quantity of oxidised iron occuring in the sediments is such as to give a significant driving force (during iron oxyhydroxide reduction) to aid the dissolution of these clay minerals[98]. Against these advantages must be placed the uncertainty of assuming limited diffusion in such wet sediments, and the relatively high level of organic matter to be found in the cores.

Unfortunately insufficient sample was available to analyse for magnesium ions, or indeed to obtain a sufficiently comprehensive analysis to allow any estimation of localised ionic strength. Thus the analyses used are in concentration units and not activities, as would obviously be more desirable. Figure 5.19 plots dissolved aluminium against silicon for the upper horizons of cores 12, 16, and 35 of 1983 and core 39 of 1985. It will be apparent that a significant inverse relationship exists. Harder[101,102] considered that where the level of dissolved iron was locally enhanced, high-Fe clay minerals, atypical of those occuring in other segments may form. Situations where the iron level was >0.5 mg l^{-1} are indicated on the

figures but scatter due to this effect is not noticeably significant. For equilibrium to exist the aluminium concentration must also be related to pH. Figure 5.20 illustrates the inverse relationship obtained. Considering the differences in environmental conditions found in these cores in terms of reducing nature and particularly with regard to the changed elemental supply and pH of the 1985 core, the consistency shown by these results is encouraging. It is also very likely that the microenvironments sampled are unstable relative to the deeper, more consolidated cores used in other studies[100], and in particular with regard to the oxidation-reduction instability that exists.

It is not possible, without the availability of ionic strength (and thereby activity) and of major cation concentrations (particularly magnesium) to attempt to quantify these findings. It does, however, provide good circumstantial evidence for the rapid generation of authigenic aluminosilicate production within these cores.

5.7.3.2. MODE OF FORMATION OF CLAY MINERALS.

This section proposes an hypothesis to explain the ratios of clay mineral forming elements found in the upper layers of cores 14, 39, and 45. Additionally core 39A is also considered. It covers a period of time ranging from near-neutral pH loch water to a final pH 10.3, and from a relatively low input of leachate to an input that, from Chapter 7, will be seen to have been having an increasingly devastating effect on the loch fauna and flora.

The formation of calcium carbonate within the loch will have

FIGURES 5.19. & 5.20. Correlations within interstitial waters.

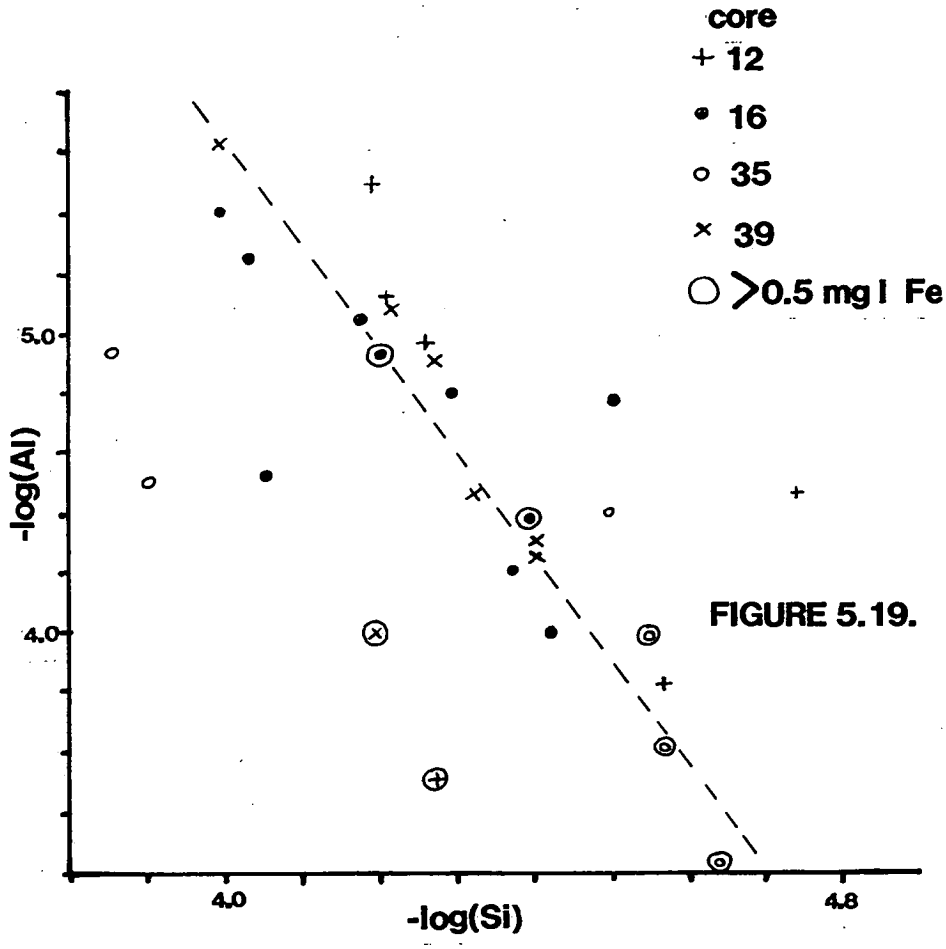


FIGURE 5.19.

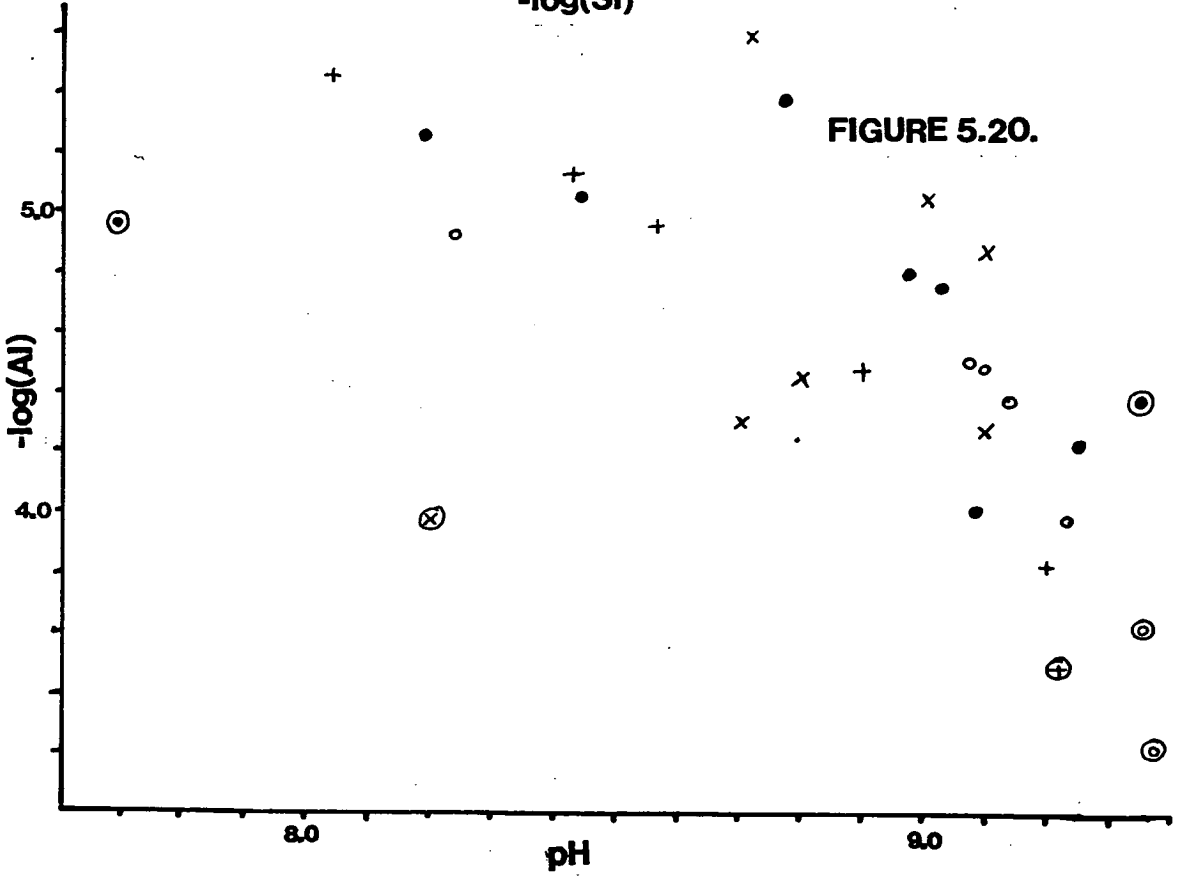


FIGURE 5.20.

gradually increased with an increasing input of sodium carbonate. However at some point in time the supply of calcium ions in the north inlet became inadequate to deal with the carbonate and the level of carbonate formation stabilised. A break occurs in the observed pH of the loch (Figure 4.4) between 1978 and 1980 when the rate of pH change increased and when the loss of macrophytes became evident. It is probable that this time represented the effective exhaustion of available calcium. Figure 5.21. illustrates the concentration of Ti and Ca throughout the red and red-brown section of the cores. For an increasing supply of carbonate and clay minerals, a constant flux of detrital titanium would yield a curve as obtained for cores 14 and 45. Core 39, being very close to the leachate inflow, will have been subject to wide variation in detrital input and receive a disproportionate quantity of heavier material. Core 39A, in particular, gives a distorted picture of detrital input due to the extremely soft mud surface. The downward trend in titanium level is matched by a general upward trend in calcium which appears to start to level off in the most recent sediments. Figure 5.22 plots the abundance of Fe, Mg, Al, and Si in the upper part of the cores. Iron displays a similar trend to titanium as may be expected by its basically detrital origin. Again the situation is confused in cores 39 and 39A.

According to Reyes et al[103] most freshwaters are in steady state when the ratio of concentrations Si:(Mg+Al) approximates to unity. From Table 4.4 it will be seen that the ratio of the elements being input to the loch was Si:Al:Mg of 0.3:0.7:1. The (post-depositional) ratio at the outlet to the loch was found to be 0.2:1.4:1 (Table 4.5). Thus the loch was evidently deficient in silicon relative to

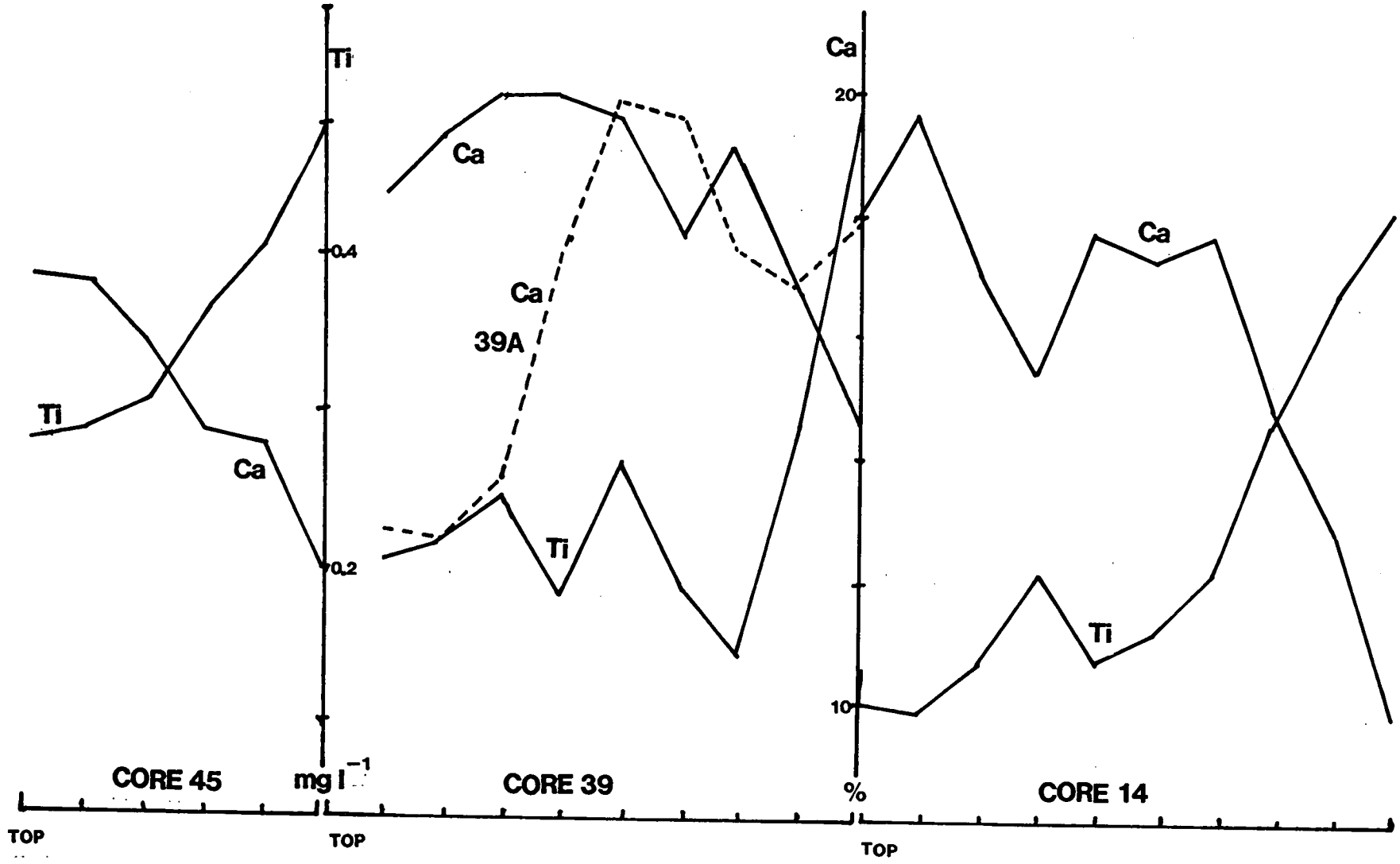


FIGURE 5.21. Concentration of calcium and titanium in upper parts of cores.

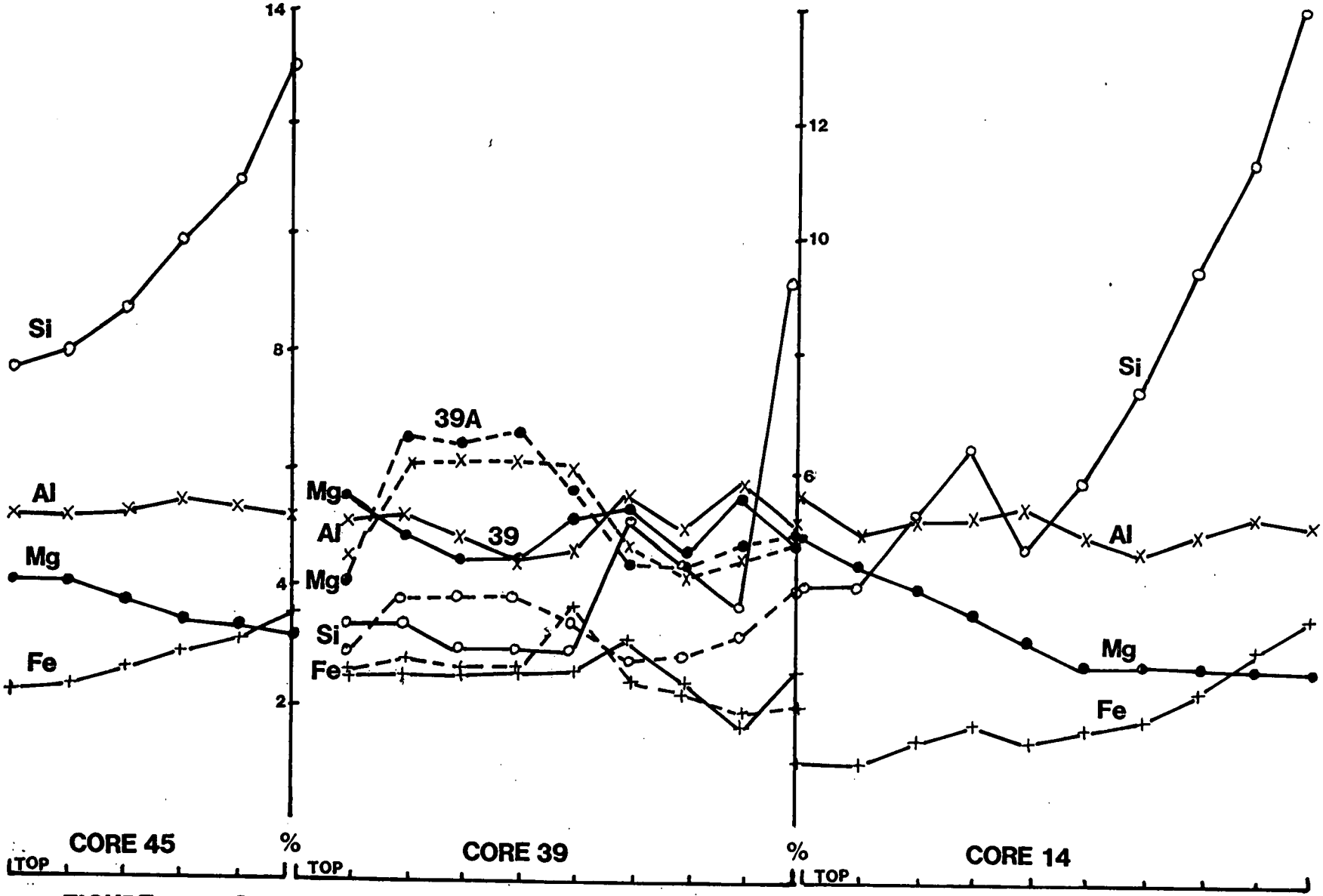


FIGURE 5.22. Concentration of elements in upper parts of cores

magnesium and aluminium. The losses calculated in Table 4.6 for the period 1981-1983 gives a Si:Al:Mg ratio going to the sediment of 0.2:0.6:1 indicating that the trend illustrated for core 14 in Figure 5.22 had continued to accelerate with deposition of Al and Mg, but in particular Mg, outstripping that of Si.

Reyes et al[103] synthesised clay minerals at normal temperatures and pressures from stepped ratios of Mg:Al for a silica content such that Si/(Al+Mg)=1. The syntheses were performed over a range of pH values. The Si ratio was higher than observed in Kinghorn Loch where Si:Mg ratios of the order of 1:5 were found. The concentration of components used were of the same order as those found in the loch. The development of the polluted state of the loch may be divided into the following four phases.

(1) Pre-polluted state. It is assumed that the loch will have had a chemical speciation similar to the north inlet water, and indeed similar to the state that has developed since the removal of the leachate. The water, at pH 7.3-8 would have contained 0.25 mmol l^{-1} Si, 0.65 mmol l^{-1} Mg, and 0.0001 mmol l^{-1} Al in solution. At this pH, using the thermodynamic data contained in Truesdell and Jones[10] it is evident that there is no inclination to precipitate any hydrous magnesium silicates.

(2) Early development of the polluted state. The introduction of only 0.01 mmol l^{-1} Al would result in the solubility product of several aluminosilicate minerals being exceeded at pH 8.5. Reyes et al[103] found that at pH 8 clays formed with an elemental ratio of Si:Al:Mg of 40:0.4:1 at Mg/Al=100 and with a ratio of 8:2.2:1 for

Mg/Al=5. The ratio found in the lowest segments of the red-brown layer in Kinghorn Loch was 5.7:2.1:1 for core 14 and 4.1:1.6:1 for core 45. This compares very well with that reported for the experimental ratio for an input of Mg/Al=5 given the lower Si content of the loch water. It is apparent from Reyes et al[104] that at this pH clay minerals of the class palygorskite or beidellite are likely to be formed. In a magnesium rich environment provided by a slightly elevated pH, the development of mixed layer clay minerals, particularly of chlorite-montmorillonite, becomes more likely and important (Weaver & Pollard[105]).

(3) Maximum development of the polluted state that is indicated in the sediments. Because of the excessive wetness and considerable reworking of the most recent sediments the uppermost segment of the cores has not normally been included in this consideration. Thus the core record will have ceased a some time before 1983 and will, in any case, due to reworking, represent a mean position over a period of time. It will not represent the apex of development of the polluted state. Reyes et al[103] noted that at higher pH levels Mg became more abundant in the precipitate relative to Al and that both elements increased relative to Si. Thus for a Si:Al:Mg ratio of 2:1:1 it was found that a precipitate formed which, on aging, gave a ratio of 5:3:1 at pH10 and 1.6:0.9:1 at pH11. The element ratio initially present in the loch water at pH10.3 was Si:Al:Mg of 0.3:0.7:1. The ratio found in the sediments was 0.9:1.2:1 for core 14 and 1.9:1.3:1 for core 45. These ratios are similar to those reported by Reyes et al[103] when consideration is given to the somewhat different input concentrations. Further, during the formation of chlorite-montmorillonite mixed layer clay minerals, brucite [$Mg(OH)_2$] layers

may form between the smectite layers by a process that would be progressive with pH[105], because of the increasing insolubility of brucite and because of the relative electopositiveness of brucite in maintaining minimum charge and therefore volume to the mineral. Weaver and Pollard[105] report that individual mixed layer do not form but rather that the process is continuous comprising all possible ratios.

The upper segments of cores 39 and 39A, due to thorough reworking, will consist of the redistributed product of several years of clay mineral formation. However this redistribution would have allowed the clays to re-establish equilibrium with the increasing pH and to form a more uniform sediment, equilibrated to pH 10 or higher, than would be found in cores 14 and 45. The ratios in cores 39 and 39A are remarkably consistent. For material taken from the 30-180 mm horizon in core 39 the ratio Si:Al:Mg was 0.94-1.11:0.61-0.71:1 and for the 0-660 mm horizon of core 39A it was 1.04-1.07:0.59-0.71:1. These ratios contain a high Mg relative to Al and Si and is indicative (Reyes et al[103]) of a precipitating environment with a pH in excess of 11. In the immediate vicinity of this station such an elevated pH has been observed.

(4) Apex of development of polluted state. As has been stated an acceleration in the rate of increase of loch pH occured from 1978 onwards. Given the levels of Mg in the loch water, then at pH 10.3 the solubility product of brucite (as given by Truesdell and Jones[10]) is exceeded. In addition, the solubility product of several magnesium silicate minerals such a sepiolite and talc are exceeded and, dependent on kinetic considerations and the supply of silica,

either brucite or hydrous magnesium silicates may form in addition to possible mixed layer clay minerals.

According to Reyes et al[104] it is likely that a palygorskite series mineral would form under similar conditions to those observed. However such a series would require a higher ratio of Si to be present. Grimm[106] gives an ideal cell composition for end member attapulgite of $(OH_2)_4(OH)_2Mg_5Si_8O_{20}.4H_2O$ where 1.5 atoms of Mg may be substituted for 1 of Al. Also some substitution of Al for Si is probable. However this author considers that extensive lattice substitution is not possible without ensuing structural weakness. Thus it is evident that for the situation at or just below pH10.3 the observed elemental ratio cannot be explained purely in terms of magnesium aluminosilicate mineral formation and must represent the generation of a mixed mineral composition. For situation (4) above silica deficiency is even more pronounced.

However, in a study of authigenic mineral formation, Mackin and Aller[100] proposed that high aluminium clays, of dioctahedral chlorite type, were being formed in nearshore sediments of the South China Sea. They proposed a formula of $EX_{.91}Mg_{.77}Al_5Si_{2.7}O_{10}(OH)_8$, where EX is an exchangable cation. Swindale and Fan[107] reported the formation of authigenic dioctahedral chlorite on detrital gibbsite [$Al(OH)_3$] in sea water. Chlorite is interpretted as being a product of early diagenesis of iron oxyhydroxide[100]. However trioctahedral chlorites are probably more stable at pH values in excess of sea water although stability field data is not available[100]. According to Weaver & Pollard[105] magnesium substitution of aluminium in octahedral sites, and aluminium substitution of silicon in terahedral sites is allowed,

such as to give a general formula for dioctahedral chlorites of $EX_eMg_xAl_{4.4-x+y}Si_{4-y}O_{10}(OH)_8$ where e monovalent cations or e/2 divalent cations balance the ionic charge. Thus this mechanism provides a possible low silica phase with excess magnesium going to brucite at very high pH.

Taking the data for losses to the sediment contained in Table 4.6 it is apparent that the ratio is Si:Al:Mg of 0.2:0.6:1. This ratio is based on several assumptions and approximations as to flow regime and original water chemistry and will not be very accurate. Also elements going to the sediment will be considerably affected by the associated precipitation of carbonate mineral and the high flux of organic material.

5.7.3.3. STRUCTURE OF CLAY MINERALS

I am grateful to Professor M. Russell of the University of Strathclyde Department of Applied Geology for work carried out by his department on my behalf. The following freeze-dried samples were subjected to mineralogical analysis:

core	depth (mm)		
	recent	intermediate	"natural"
12	60-90	90-120	210-240
14	90-120		540-560
16	60-90	120-150	240-270
35	60-90	180-210	240-270

Small quantities of clay minerals were found and attempts were made to concentrate these. Treatment with 10% hydrochloric acid appeared to destroy a significant amount of clays, but 10% acetic acid was found to conserve them and allow concentration. Two clay components were found. A component at 7-8 Å was unaffected by glycolation and

rendered amorphous by heating to 600°C. This behaviour is typical of non-expanding clays such as kaolinite which gives a peak at 7.15 Å. The other component was situated at 14-15 Å. This peak moved to 15.79 Å on glycolation and to 13.33 Å on heating to 300°C. The behaviour is typical of an expanding clay. It is not known whether the structures found relate to detrital inputs or to crystalinity formed within the loch. The depositional time-scale is so short that the former source must be considered more likely.

5.7.4. ORGANIC CARBON AND RELATED ELEMENTS.

5.7.4.1. OXIDATION-REDUCTION PROCESSES.

Supply of organic carbon to the sediment arrived by two routes. A small component of 10-40 g m^{-2} yr^{-1} (as CH_2O) occured by way of dissolved humic material in the north inlet water, combined with an indefinable, though probably small, contribution from macrophyte debris, ground seepage and tree-leaf detritus (see Chapter 4.7.4). The major component however, some 200-300 g m^{-2} yr^{-1} (as CH_2O), was autochthonous, the debris of high level production by phytoplankton. Most of the labile phytoplanktonic debris is recycled within the water column (see Chapter 4.7.4) and the detritus reaching the sediment is found to be enriched with organic carbon relative to nitrogen and phosphorus. At times, when deeper waters became anoxic, more of the relatively labile material will have reached the sediment. Aerobic digestion at the mud-water interface is highly efficient but for Kinghorn Loch this process should have been limited, the sediments being so reducing as to allow only anaerobic digestion (see Table 5.9).

The ratio of organic C:N is indicative of the 'refractory' nature

(i.e. degree of humification) of the organic component and Figure 5.23 illustrates the ratios found for cores 14, 39, and 45. Fresh phytoplanktonic protoplasm contains C:N ratio of 5.7:1 (Chapter 4.7.4) while for water soluble humic colloids from peat (dopplerite) C:N is 46-52:1 and for Sphagnum is approximately 35:1. Degens and Mopper[108] consider in detail, and by diagramatic illustration, the structure and sorptive processes occuring through humic compounds and should be referred to for further information. Humic material is considered to dominate for C:N >10 (Wetzel[21]).

For core 45 the ratio is initially low indicating the freshness of material due to the shallowness of the water at this station. However within the upper 120 mm some 30% of the organic matter is lost and the C:N ratio increased to 12, which is higher than attained for core 14, indicating more comprehensive degradation. A check on Table 5.9 indicates that the upper 10-20 mm of core 45 remain reasonably oxic in character. The C:N ratio within core 39 is high and considered to be caused by detrital humic material being brought in with the leachate rather than by phytoplanktonic contribution. The drop in ratio with depth is indicative of a more natural condition prevailing at this station in the past. The situation for core 14 is one of little change. Even though analysis of the 0-30 mm was available there is no indication of fresh phytoplankton debris being present. However cores 14 and 39 both lose some 15% of their organic carbon content within the top 60 mm. Thus it is evident that organic debris was extensively degraded before reaching the interface within the deeper parts of the loch.

Bacterial populations are responsible for the degradation of the

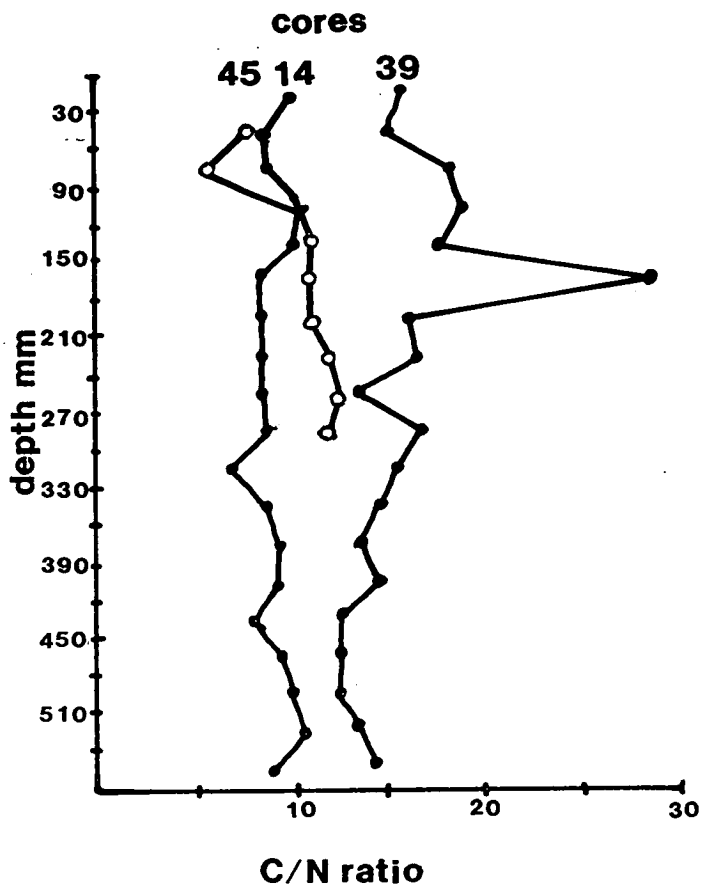


FIGURE 5.23. Ratio of C:N down cores.

organic material and are found in greatest numbers at the mud-water interface[21]. As saprophytic bacteria decrease rapidly with depth in the sediment it is considered that assimilable organic material also decreases rapidly. Processes in the sediment increase greatly in rate with temperature[21].

Under anaerobic conditions an electron acceptor is required in order to drive the degredation. Several exist in the system under consideration including abundant Fe(III) and sulphate and a certain amount of nitrate. Carbon dioxide is also available as a result of methane production. The following half cells may be identified, with due regard being given to dominant speciation at pH 10, and values of the equilibrium constant, K, are given for 25°C:

$1/5.NO^-_{3(aq)} + 6/5.H^+ + e \leftrightharpoons 1/10.N_{2(g)} + 3/5.H_2O$ log K = 21.03

$1/8.NO^-_{3(aq)} + 5/4.H^+ + e \leftrightharpoons 1/8.NH^+_{4(aq)} + 3/8.H_2O$ log K = 84.95

$1/8.SO^{2-}_{4(aq)} + 9/8.H^+ + e \leftrightharpoons 1/8.HS^-_{(aq)} + 1/2.H_2O$ log K= 24.0

$1/8.CO_{2(g)} + H^+ + e \rightleftharpoons 1/8.CH_{4(g)} + 1/4.H_2O$ log K = 16.34

$1/2.Fe_2O_{3(c)} + 3H^+ + e \rightleftharpoons Fe^{2+}_{(aq)} + 3/2.H_2O$ log K = 63.29

It is generally found that the order of these processes occuring in marine waters at neutral pH tends to be nitrate reduction, followed by sulphate reduction and methane generation (Richards[109]). Concentrations of species listed above will be in a similar relative order in the initial composition of Kinghorn Loch interstitial water and the order may therefore be expected to be similar for the loch. pH has a similar effect on these reactions and at pH 10 the reaction order will remain[22]. However the Eh at which these reactions occur are greatly reduced at pH 10. Nitrate[21] and sulphate[110] reduction processes are indicated by the following reactions.

$$5(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 424NO_3^-$$
$$= 212N_2 + 31CO_2 + 499HCO_3^- + 5H_2PO_4^- + 80NH_4^+ + 243H_2O$$

$$(CH_2)_{106}(NH_3)_{16}H_3PO_4 + 53SO_4^{2-}$$
$$= 38CO_2 + 68HCO_3^- + 53HS^- + 16NH_4^+ + H_2PO_4^- + 38H_2O$$

Nitrate reduction occurred in core 39 taken during 1985 where the interstitial water contained <0.1-0.3 mg l^{-1} compared to 6.3 mg l^{-1} N in the water body. During 1983 nitrate content of the water body was so low (0.2 mg l^{-1}) as to indicate either total assimilation to the biomass or prior denitrification. Table A.10 indicates that a complex situation existed with low levels in the water body and elevated levels at the mud-water interface due to nitrate release. Sulphate reduction is not exhaustive in the interstitial waters and only up to 50% has been removed by reduction, even at the lower pH values found in the upper parts of core 39 in 1985. In fact, Figure 5.24 indicates a lack of uptake of sulphate by organic material, even though over the same period sulphate levels in the loch water will have increased. Ingvorsen et al[111] found that considerable reduction of sulphate occurred in Lake Mendota, Wisconsin, at the interface where a level of 6 mg l^{-1} S was turned over in 10-24 hours. These workers found that sulphate did not readily utilise fatty acids. Kuivila and Murray[112] found that sulphate reduction occurred in narrow bands in the sediment separated by diffusion zones and found that in Lake Washington sediments the C:N ratio fell from an initial 3.9 to >14 at 500 mm. They found that alkalinity increased with depth and that this was related to ammonia production and the reduction of iron. The top deposits were very nitrogen rich, unlike in Kinghorn Loch, where the generation of ammonia would be much more limited.

A major process for the removal of large quantities of organic matter is by methane fermentation which generates quantitative amounts of carbon dioxide and methane by internal electron transfer processes[21]. The process occurs within a highly reducing microenvironment and so may bypass Eh priorities. The reaction is represented as follows.

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 53H_2O = 53HCO_3^- + 53CH_4 + 16NH_4^+ + HPO_4^{2-} + 39H^+$$

The initial reaction is by hydrolytic rearrangement to fatty acids, 70% of which is acetic acid, followed by further rearrangement to break the molecule to carbon dioxide and methane. Higher hydrocarbons are not generated by this process[22]. The energy released generates cell material. Methane production is often so great as to cause escape to the water body where most is recycled by methane oxidising bacteria. During 1984, when the loch waters became very clear, gas production within the shallow sediments was evident. This process recycles ammonia and phosphate and generates small quantities of hydrogen. A wide range of organic hydrogen donors or hydrogen may reduce the liberated carbon dioxide to methane.

Cellulose is also readily decomposed by this process but the acidic fermentation products are found to inhibit bacterial metabolism[21]. This may be offset to some extent by the ammonia produced. It is common for very low pH values to develop in the sediment[22]. In Kinghorn Loch this generation of acidity has two effects. Calcite is immediately dissolved to release calcium and bicarbonate ions into the interstitial water. Material coated onto, or enclosed within the calcite will be released issuing iron, phosphate and arsenic from hydrous iron oxides and silica and aluminium from clays. Dissolved iron will be liable to reduction and form FeS or FeS_2 with HS^-

released from organic matter or by sulphate reduction. This reduction in pH associated with increases in interstitial concentrations of the above mentioned determinands is seen throughout the data illustrated in Tables 5.18 and 5.19. The reduction in pH may locally bring into operation lower priority electron acceptors and cause a range of reactions to be occuring within the sediment at similar Eh values. Thus it will be seen that reduction of organic matter provides the pool of electrons necessary to drive these mobilization reactions in the sediment.

For a eutrophic lake the release of methane and hydrogen from the sediments may further deplete oxygen levels thus allowing more organic material to reach the sediment and thereby increase gas production further[21]. Most of the products of reduction processes are dissolved species (e.g. NH_4^+, $H_2PO_4^-$), or gases (e.g. N_2, CO_2, CH_4) while other components become fixed (e.g. FeS,FeS_2, humic compounds). In this way sediment mass is reduced and diffusion pathways may be improved. Humification causes a >50% reduction in the organic mass[21] and acidification during methane production may reduce the mass of calcite. The release of dissolved organic matter to anoxic water layers may become measurable[21]. Nitrogen and phosphorus are released into the water body, although much of the phosphorus will be redeposited by reoxidation of iron. Between pH 8-9.5 sorption onto clays and hydrous iron oxides occurs readily but toward pH 9.5 increasing quantities of phosphorus escape due to the increasingly negative surface charge developing on the substrate. Above pH 9.5 release is reported to decrease rapidly and Martynova[113] postulated that phosphate would co-precipitate with acid-released calcium ions to form basic calcium phosphate precipitates.

Remobilised phosphate is known to diffuse from considerable depths in the sediment (>100 mm)[21]. Macrophytes are very efficient recyclers, and excrete phosphate from roots and leaves[114]. Although data for phosphate is incomplete it is evident from Table 5.18 that the level of soluble phosphate in material liable to turbation (8.3 mg l^{-1} for core 12) is greatly in excess of that found in the water body (0.1 mg l^{-1}) and recyling obviously occured. Activity in the samples taken in July 1983 is greatest in the top segments whereas the core taken in April 1985 shows a more general activity throughout the area of changing pH and is probably related both to the pH profile and the less reductive environment indicated by the Eh^* profile (Table 5.9).

In conclusion it must be considered that although Kinghorn Loch sediments are moderately rich in organic matter and abundant in electron acceptors, particularly Fe(III) and sulphate, and that Eh^* values were very low, reduction processes were not carried to completion. Total exhaustion of iron and sulphate and gross production of sulphide did not occur, unlike that reported for many other lakes[e.g.112]. Two factors appear to restrain the processes, the first being the high initial C:N ratio found, indicating a higher degree of humification, perhaps due to slower settlement rates caused by surface charge effects. Secondly the highly buffered, high pH value of the interstitial waters would demand a much lower Eh in order for reduction to occur.

5.7.4.2. HISTORY OF DEPOSITION.

Figure 5.24 suggests that a complex series of events have led to the development of the organic profile shown in the cores. The hypothesis which follows attempts to explain the evident peculiarities in elemental distribution. The physical zones are used to divide the events.

(1) Dark grey-black fibrous material.

The quantity of organic material being deposited during this period was small compared to later years as the rate of deposition was very low (see Chapter 5.6). The body of the material consists of degraded plant remains and shells and will have been derived mainly from terrestrial sources and littoral macrophytes. These materials will have been richer in sulphur than the later phytoplanktonic debris. C:S ratios in this zone vary from 3:1 to 10:1 with a mean of 4:1. Degraded marine sediments contain a mean ratio of 2.8:1 (Berner[115]) while for lakes the ratio varies according to sulphate level from 1.4:1 if sulphate rich to 92:1 if sulphate poor (Nriagu and Soon[116]) with sulphur inclusion becoming significant for sulphate-S levels in the water of >5 mg l^{-1}. The level of carbon and sulphur is found to increase towards the upper boundary of the zone and probably indicates an increase in macrophyte growth due to the rich supply of nutrient phosphorus being provided by the infant flow of leachate. However the C:S ratio remained of the order of 3:1 despite the increase in sulphate supply. Thus a period of prolific macrophyte growth would be seen with a subsequent increase in organic nutrients and carbon in the sediment. Ultimately however this eutrophication leads to an increase in plankton at the expense of littoral

macrophytes[21] and in Kinghorn Loch this change would have been aided by toxic effects, which by 1983, had caused a virtual absence of macrophytes in the loch.

(2) Fine grained grey zone.

The colour of this zone presumably indicates the presence of abundant mineralised sulphur. It is unfortunate that time has not allowed a thorough examination to be carried out. The texture is similar to that above it, and with the exception of a few shells, shows little similarity to the material below. However the chemical characteristics of this material are similar to that below and not to the physically similar material above. This statistical similarity must reflect the gross level of organic elements and iron that occurs here. The maximum levels of sulphur, carbon, and nitrogen are found in this zone and is indicative of a prolific flora, but few plant remains exist. It can be postulated that by this time the littoral supply had been superceded by a mixed planktonic community, much more diverse than in later years. Detritus of zooplankton and benthic invertebrates may have maintained a varied elemental input for a time. Also a rich bacterial population would continue to work the organic material below and cause redistribution into the upper band. Wetzel[21] considers that this humification process results from the bacterial redistribution of sulphur, virtually all of which is assimilated by the bacteria before being used to form C-S bridges during humification. Sulphur mineralisation will have occured in the newly created, more reductive surficial sediment at near-neutral pH and slightly positive Eh values[21]. The sediment of some eutrophic lakes such as Lake mendota, Wisconsin, appear to contain negligible quantities of pyrite while organic material accounts for >45% of sediment

sulphur[117]. This is possibly because of the loss of hydrogen sulphide from the sediment at neutral pH. Berner[118] states that sulphur mineralisation only occurs to any significant extent near the mud-water interface and not far below. Thus a modest covering of less organically rich sediment at higher pH would result in a drop in mineralisation. Station 39 will have seen the most dramatic effects, since considerable macrophyte growth occured in this area at one time, whereas station 45 is close to a grassy hillside with rocky shores. This isolation from the main sources of material for reworking may have prevented the development of a grey zone in core 45.

(3) Red-brown fine grained zone.

Inclusion of sulphur into the sediment decreased rapidly and the existence of sulphate and iron(III) in this zone probably resulted from the difficulty of initiating reductive processes at the high pH that was developing. It also appears that plankton debris, by this time apparently restricted to Oscillatoria, seems to have been low in sulphur but rich in phosphorus. The sulphur content of biota varies from 0.02%-2% relative to carbon content with a mean of 0.08%[21] and "algae" found in Lake Windermere[11] contained 0.02%. Nriagu[117] reported 0.8-1.0% sulphur (of total dry weight) in macrophytes of Lake Mendota with 0.65% in combined plankton.

(4) Red thixotrophic zone.

This zone represents the physically mixed material and is the site of most of the active reduction processes. Its origins would have been similar to that below it.

5.7.4.3. CORRELATION BETWEEN ELEMENTS.

Considering the different sources of organic material that has gone to create the sediment, and the different processes at different pH's that have created its degradation, it is not surprising that none of the elements are found to be correlated in the upper parts of the cores (Table 5.17). The correlation of organic carbon with copper will be examined in Chapter 5.7.6. Figure 5.24 illustrates that phosphorus increased to a plateau in recent times while carbon and nitrogen, which show a reasonable correlation overall, decreased to a plateau while sulphur decreased sharply. The overall correlation of carbon and nitrogen will be due to their association in the humification process.

Phosphorus may take part in other reactions leading to its deposition, such as sorption onto clay minerals and hydrous iron oxides as well as phosphate coating on calcite. Figure 5.25 shows scatter diagrams for the relation between phosphorus and various other elements in the upper parts of the cores. It will be noted that no correlations exist in any instance.

5.7.5. IRON AND REDOX SENSITIVE ELEMENTS

Goethite or hematite crystalinity has not been observed in the loch sediments even though the red to red/brown colour of the upper sediments is indicative of the presence of minerals with Fe(III) predominating[119], such as iron oxyhydroxide or ferric smectites. The level of iron in the sediment is approximately 2.5% and should be adequate to allow the determination of any crystallinity present. However, if only the finest particles of the red mud were washed into the loch then the mineral may have been in an amorphous state. Also

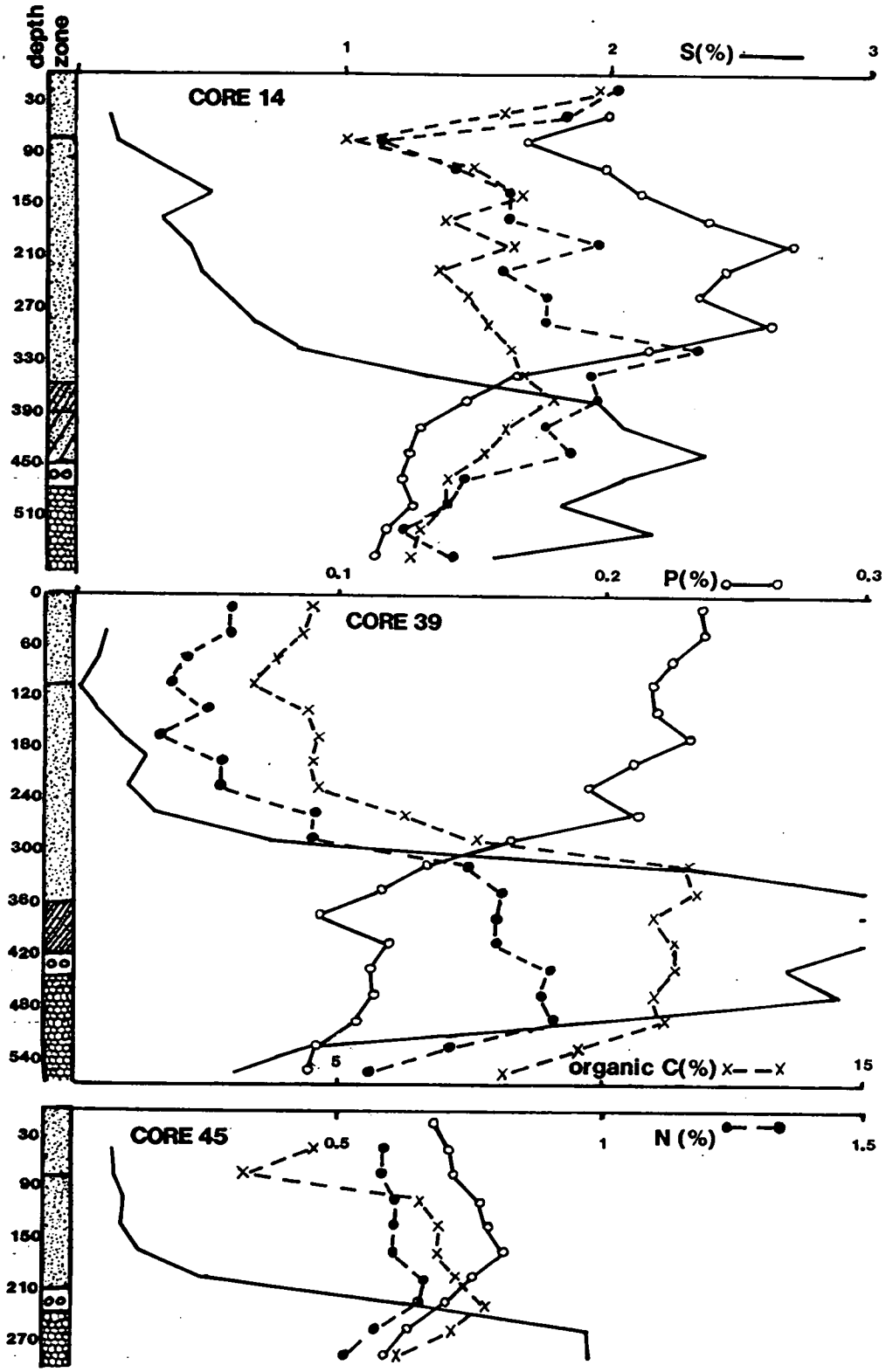


FIGURE 5.24. Concentration of organic carbon and related elements

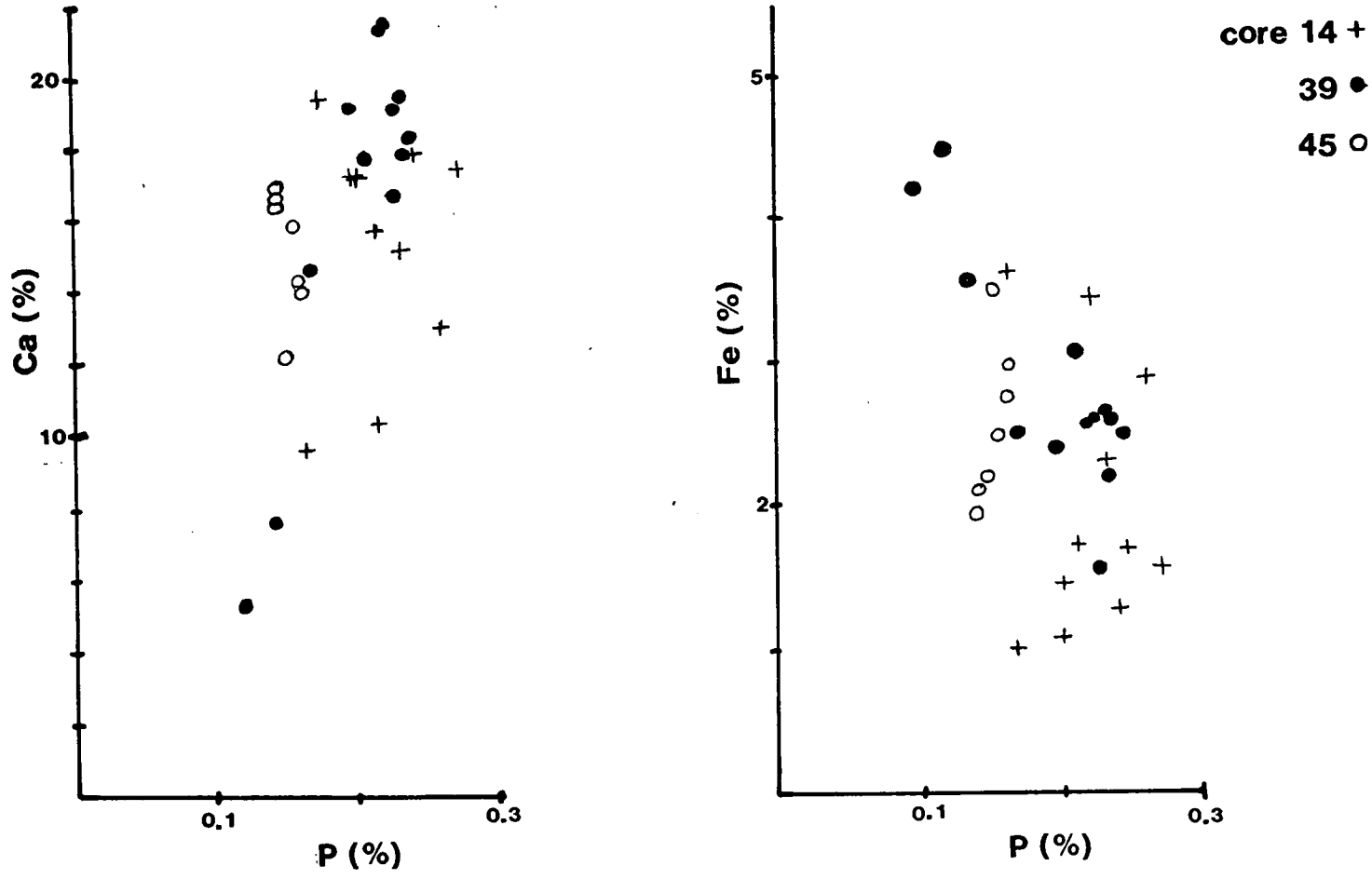
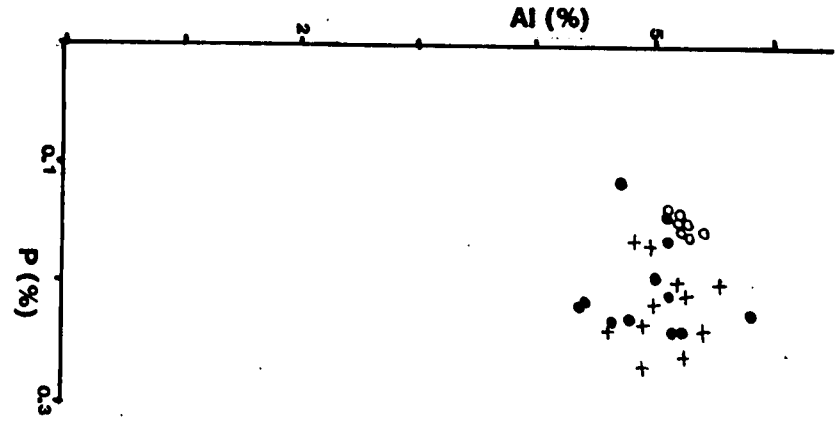
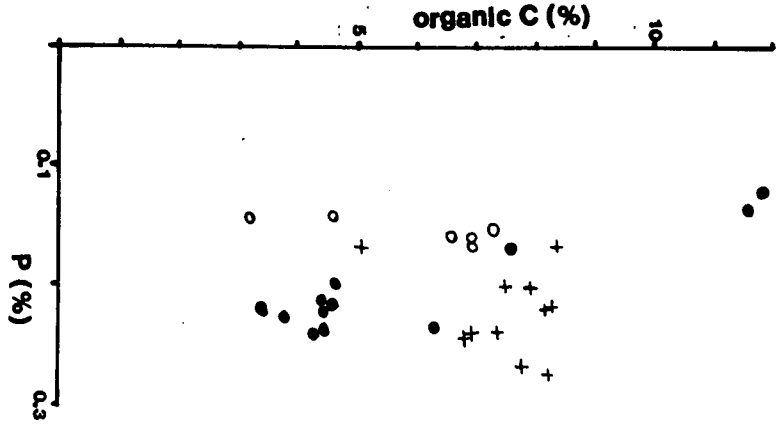
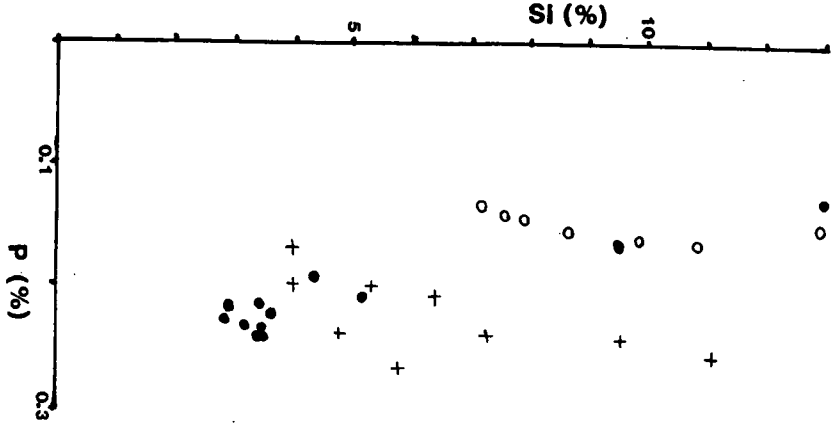
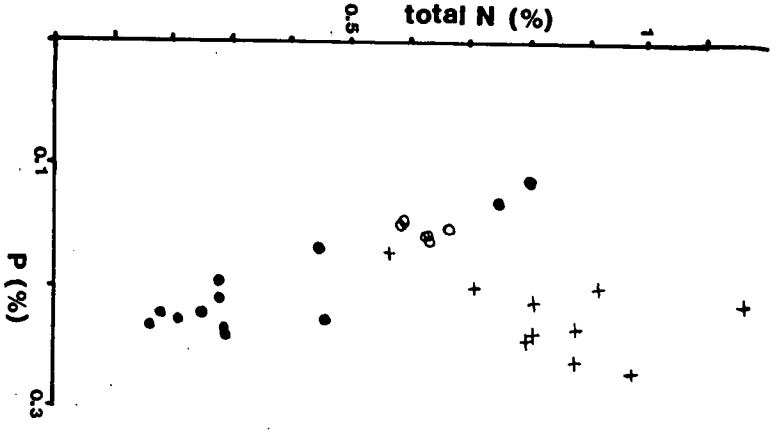


FIGURE 5.25. Correlation of phosphorus and other elements in the upper parts of cores


Al (%)
2
5
P (%)
0.1
0.3


organic C (%)
5
10
P (%)
0.1
0.3


Si (%)
5
10
P (%)
0.1
0.3


total N (%)
0.5
1
P (%)
0.1
0.3

any alteration during deposition, such as incorporation in phytoplankton, would destroy the crystallinity. However, the Fe(III)-Fe(II) reaction in smectites is reversible (Russell et al[120]) and it is energetically more favourable for ferrous ions to be incorporated in clay mineral structure than ferric ions[37]. Thus on the reduction of hematite, ferrous ions may be incorporated into clays only to be oxidised to the ferric clay structure. Mackin and Aller[98] and others consider that such substitutions would be unstable during the formation of minerals such as α-FeS or pyrite. However, Mackin and Aller[100] do consider that lattice replacement may well occur for residual ferrous ions at deeper depths in sediments if the sulphur supply is sufficiently restricted. Mg^{2+} appears to be enriched in the clay mineral phase of these sediments relative to marine situations and by consideration of Tardy and Garrels[37] it appears that the replacement of Mg^{2+} with Fe^{2+} would be favoured. Russell et al[120] have suggested that only 10% of the iron in smectites needs to be reduced to cause a colour change to grey or grey/green.

It is evident from Garrels and Christ[9] that hydrated iron oxides are increasingly stable under reducing conditions as the pH of the solution rises. Several reactions have been considered below using standard free energy values taken from Stumm and Morgan[8], except for α-FeS obtained from Garrels and Christ[9]. The reactions have considered only the precipitated forms of iron in order to avoid any conjectored concentration for Fe^{2+}. Hematite has been used but goethite would yeild very similar values. The activities of carbonate, sulphate, and silicate have been taken from the three year mean concentrations in the loch water (Table A.5) combined with activity coefficients calculated from the speciation model (Chapter

6). This consideration does, of course, assume the presence of a suitable electron donor half cell. Ion activities used are:

ion	activity
CO_3^{2-}	2.6×10^{-3}
SO_4^{2-}	7.7×10^{-4}
$H_4SiO_4^o$	4.3×10^{-5}

Then for

$$Fe_2O_{3(c)} + H_2O_{(l)} + 2H^+_{(aq)} + 2e \leftrightharpoons 2Fe(OH)_{2(c)}$$

the standard free energy of the half cell reaction is

$$\Delta F^o_r = \Delta F^o_{fFe2O3} + \Delta F^o_{fH2O} - 2\Delta F^o_{fFe(OH)2}$$
$$= -6.68 \text{ kJ mol}^{-1}$$

and from $E^o = \Delta F^o / n\mathcal{F}$, where n = no. of electrons participating in the reaction and $\mathcal{F} = 96.49$ kC mol^{-1}, the standard half cell potential $E^o = -0.0346$ volts

Then the half cell oxidation potential

$$Eh = E^o + [\, RT \ln(\text{product oxidised/reduced activities})]/n$$

where $R = 0.008314$ kJ mol^{-1} K^{-1} and $T = 285$ K

so $Eh = -34.6 - 56.5pH$ (in mV).

Similar expressions may be found for the following transformations, with Eh in mV and the material state taken as crystalline, liquid or aqueous as appropriate.

(1) $Fe_2O_3 + H_2O + 2H^+ + 2e \leftrightharpoons 2Fe(OH)_2$

$Eh = -34.6 - 56.5pH$

(2) $3Fe_2O_3 + 2H^+ + 2e \leftrightharpoons 2Fe_3O_4 + H_2O$ (magnetite)

$Eh = 177.6 - 56.5pH$

(3) $Fe_2O_3 + 2CO_3^{2-} + 6H^+ + 2e \leftrightharpoons 2FeCO_3 + 3H_2O$ (siderite)

$Eh = 1277 + 56.5 \log(CO_3^{2-}) - 169.5pH$

(4) $Fe_2O_3 + H_4SiO_4^o + 2H^+ + 2e \leftrightharpoons \underset{\text{fayalite}}{Fe_2SiO_4} + 3H_2O$

$Eh = 163 + 28.3 \log(H_4SiO_4) - 56.5pH$

(5) $Fe_2O_3 + 2SO_4^{2-} + 22H^+ + 18e \rightleftharpoons 2FeS + 11H_2O$

$Eh = 337 + 6.3 \log(SO_4^{2-}) - 69.1pH$

(6) $Fe_2O_3 + 4SO_4^{2-} + 38H^+ + 30e \rightleftharpoons \underset{\text{pyrite}}{2FeS_2} + 19H_2O$

$Eh = 382 + 7.5 \log(SO_4^{2-}) - 71.6pH$

These findings are represented in diagramatic form in Figure 5.26. Note that the curvature of the siderite phase below pH 10 is illustrative only, as the carbonate equilibrium was not recalculated for lower pH values.

It is evident from the figure that hematite is a stable phase at -250 mV for pH 8.5 and above. Eh* values more negative than this occured below 30 mm (approximately) in the sediments during 1983 (Table 5.9). Interstitial pH values for the upper parts of the cores remained above or around pH 8.5 in all instances (Table 5.18). Interestingly, a lower pH appeared at the position in core 16 where a grey horizon occured, indicative of pyrite formation. It was not possible to quantify Eh* below -250 mV but it is evident that although hematite (or ferric clay minerals) was stable above the grey zone, reductive processes were occuring, as evidenced by the lower sulphate values in the interstitial waters and the existence of significant levels of dissolved iron, aluminium, arsenic and calcium (see later sections).

In core 39 taken in April 1985, pH values of interstitial waters were found to have remained elevated despite the drop in loch water pH

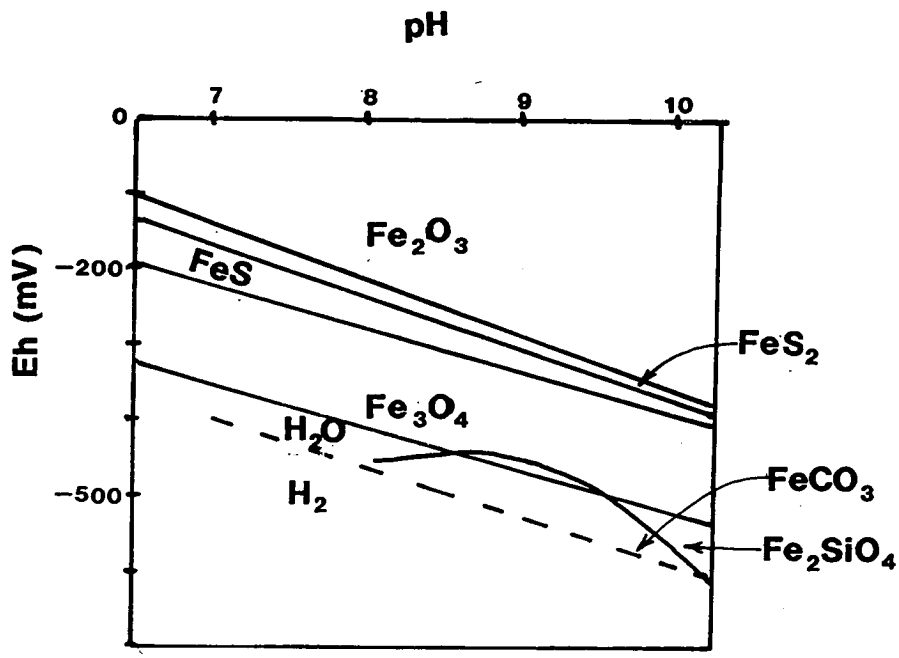


FIGURE 5.26. Stability of iron(II) minerals relative to hematite for concentrations found in Kinghorn Loch interstitial water (at 12°C).

(see Table 5.19) while the Eh* profile gave results consistently above -180 mV (Table 5.9). However, reductive processes were still occuring, albeit at a less intense level. This indicates the existence of reduction microenvironments where the Eh values must locally be well below those indicated.

Wetzel[21] states that within a freshwater lake, sulphur is generally supplied by biotic activity, with much of it originating from atmospheric input. He estimated the mean aquatic supply to be approximately 4 mg l^{-1} as S. In marine situations, sulphate reduction is responsible. In Kinghorn Loch it is evident that sulphate reduction should be the main source of sulphur to the sediment, although it will be seen that organic sulphur was also significant. As explained in Chapter 5.7.4.2 this does not appear to be the case with limited sulphur being mineralised.

5.7.5.1. ESTIMATION OF IRON SULPHIDE MINERALISATION

Using the method of Davison & Lishman[121] freeze-dried sediment was used to determine the acid volatile sulphur (A.V.S.) component of each segment. The reported procedure involves the addition of acid to 20 mg wet weight of sediment, held in a 20 cm^3 syringe, by way of a three-way tap. The acidified sample is incubated at 95°C for 2 hours and the evolved gases (and acid solution) passed, via the tap, through a filter into a syringe containing zinc acetate solution. The sulphide present is determined by colorimetry. Modifications were required in order to allow for the highly calcareous nature of the sediments and these are described in the procedure below. The method allowed the determination of 12 samples each day. The analysis of 4 replicates of core 39, 150-180 mm, indicated that

reproducibility was better than 5%.

Having estimated A.V.S. by this means it became evident that this form of sulphur, mainly as FeS, comprised only a small proportion of that present. The scheme of analysis proposed by Zhabina and Volkov[122] was employed to determine the forms of sulphur occuring. The scheme required more than one day per sample and it was decided to concentrate effort on looking for pyrite in particular, at an horizon that would indicate authigenic production. The 60-90 mm depth was chosen for cores 14, 39, and 45 while red mud was screened for detrital pyrite content. It was decided not to differentiate the forms of organic sulphur from elemental sulphur as the process was very time consuming. A.V.S. was measured as a check on the syringe method. Agreement was reasonable with results found to be 48/41, 20/32, and 15/16 (mg kg^{-1} dry weight) for Davison/Zhabina procedures for segment 60-90 mm of cores 14, 39, and 45 respectively.

(1) ESTIMATION OF A.V.S. BY METHOD OF DAVISON AND LISHMAN

APPARATUS

Required for each sample:

2x20 cm^3 and 1x1 cm^3 borosilicate glass syringe with Leur fitting.

In-line 25 mm diameter filter holder containing 5um cellulose membrane.

Disposable 3-way plastic tap.

Spectrophotometer fitted with 10 mm flow-through cell.

Oven at 60°C.

REAGENTS

Hydrochloric acid 5.93 M

500 cm^3 concentrated hydrochloric acid diluted to 1 l

Zinc acetate solution

5 g zinc acetate + 1.25 g sodium acetate dissolved in water and made to 1 l

NN-diethyl-p-phenylenediamine sulphate (DPD) solution

2 g of the salt dissolved in 100 cm^3 50% v/v sulphuric acid and made to 200 cm^3 with water

Ammonium iron(III) sulphate solution

18 g $NH_4Fe(SO_4)_2.12H_2O$ dissolved in water and made to 200 cm^3

Sodium sulphide standard solution

2.5 g (dry) sodium sulphide dissolved in 1 l water. The solution was standardised by iodine titration (Chapter 9).

METHODOLOGY

Approximately 200 mg freeze-dried sample was placed in the centre of a 100x25 mm strip of aluminium foil curved so as to easily fit inside the barrel of a 20 cm^3 syringe. The foil was placed into a weighed barrel and tilted to deposit the sample at the base of the syringe. The foil was removed so as to avoid fouling the sides of the barrel with sample. The barrel was accurately reweighed to determine sample weight. A plunger was fitted to the syringe barrel so as to allow the minimum of air space and, using a 1 cm^3 syringe connected via a three-way tap, 0.5 cm^3 of hydrochloric acid was added. The syringe plunger was allowed to push out to a gas volume of up to 10 cm^3. When gas evolution had ceased (approximately 20 min) the syringe was connected, via the tap to another syringe containing 20 cm^3 zinc

acetate solution and the excess gas bubbled into it, being careful to avoid the transfer of liquid or solids. After 10 min the syringe was separated and each closed off with a three way tap. The gas contained above the zinc acetate solution was expelled to atmosphere. The acidified sample was heated at 60°C for 30 min. After cooling the syringes were reconnected and the zinc acetate solution passed into the acidified sample. The sample syringe was connected via the tap through a filter membrane to an empty 20 cm^3 syringe. and the solution passed through the filter into this syringe. The volume was checked to be 19-20 cm^3. Using a 1 cm^3 syringe, 0.5 cm^3 of DPD solution was added and the syringe inverted several times. After 2 min, 0.5 cm^3 of ammonium iron sulphate solution was added and after 15 min but within 2 hours the absorbance was read at 670 nm. Reagent blanks and calibration standards were similarly complexed and the absorbances measured at 670 nm. Although not tested for, the L.O.D. was estimated to be approximately 4 mg l^{-1} with a precision at 95% c.l. of better than 5%. The results obtained are illustrated in Table 5.20.

(2) ESTIMATION OF PYRITE, A.V.S., AND ORGANIC SULPHUR BY METHOD OF ZHABINA AND VOLKOV.

APPARATUS.

Digestion apparatus consisted a two-neck round bottomed 250 cm^3 flask fitted with an upright condenser tube to avoid splash-over and an oxygen-free nitrogen bleed terminating near the base of the flask. The gas stream from the condenser led through two Dreschel traps each containing 50 cm^3 of zinc acetate solution. Nitrogen was passed at 2 bubbles s^{-1}, and the flask could be heated by means of a electro-thermal mantle.

Soxhlet extraction apparatus was also required.

REAGENTS.

Hydrochloric acid - concentrated and 1.5 M

0.5 M Zinc acetate solution

0.75 M Sodium carbonate solution

Acetone

95% Ethanol in water ("industrial spirit")

Chromium(III) chloride hexahydrate

Zinc amalgam (40% zinc)

Chromium(II) solution

82 g of chromium(III) chloride hexahydrate was dissolved in 300 cm^3 water + 100 cm^3 1.5 M hydrochloric acid in a 500 cm^3 flask fitted with an oxygen-free nitrogen bleed. Nitrogen was passed at 2 bubbles s^{-1} for one hour and 100 g zinc amalgam added. The open end of the Dreschel bleed was fitted with a suitable adaptor to take a narrow (approximately 1 mm) bore PVC tube to act as a restrictor and the gas flow maintained for three days in darkness. The bleed was replaced with a tapered glass stopper (a screw cap must not be used), which was lifted slightly each day to release pressure of hydrogen. After seven days the solution was found to be bright blue in colour. The solution was stable for several weeks but required the release of hydrogen pressure each day.

Bromine solution

20 cm^3 bromine was dissolved in 30 cm^3 carbon tetrachloride.

Potassium permanganate crystals ($KMnO_4$).

Concentrated nitric acid

Sodium hydroxide solutions - 5 M and 1 M.

METHODOLOGY.

Approximately 1 g of freeze-dried sample was accurately weighed into the digestion flask and nitrogen passed for 10 minutes, when 80 cm^3 1.5 M hydrochloric acid was added through the top of the condenser by temporarily disconnecting the line to the Dreschel bottles. The line was reinstated. The nitrogen flow was maintained. After approximately 20 min, when the gas release slowed, the flask was heated to boiling point and immediately allowed to cool. After a further 20 min the zinc acetate solutions were mixed in a 125 cm^3 bottle, 1 cm^3 sodium carbonate solution added and, after filling to the neck with water, the bottle was inverted several times. Sulphide was determined by the DPD method described in Chapter 9. This fraction represented the acid volatile sulphide component. The level found in a reagent blank was negligible and a LOD of 2 mg kg^{-1} was indicated.

The acidic residue from the flask was filtered through a glass fibre disc (GF/C) under vacuum and the residue washed with 3 x 20 cm^3 aliquots of water. All excess water was sucked from the disc by vacuum. The acid filtrate was neutralised to pH 4-4.5 with sodium hydroxide and made up to 250 cm^3 with water. Sulphate was determined as given in Chapter 9. This fraction represented the soluble sulphate component. The level of sulphate in a reagent blank was found to be negligible and an LOD of 300 mg kg^{-1} was indicated.

The glass fibre disc was folded so as to loosely enclose the residue and placed in a Soxhlet extraction apparatus and extracted with acetone for 16 hours. The Soxhlet extract contained elemental sulphur + some organic sulphur and this was placed in storage. The glass fibre disc with residue was dried at 70°C, unfolded and placed

in a clean digestion flask. The flask was connected to the apparatus as before with zinc acetate solution in the Dreschel bottles. 10 ml 95% ethanol was added and the nitrogen bleed attached and allowed to operate for 10 min before 50 cm^3 chromium(II) solution was added. 20 cm^3 concentrated hydrochloric acid was added through the condenser and the gas flow through the absorbers returned. When the release of gas from the sample had diminished the solution was gently boiled for 1 hour. After cooling the zinc acetate was removed and sulphide determined as before. This fraction represented the pyrite sulphur. The level of sulphide found in a reagent blank was negligible and a LOD of 10 mg kg^{-1} was indicated.

The digested disc was broken up with a glass rod and the acid residue was filtered and all solution washed from the digestion flask with water. The residue on the filter disc was washed with 3 x 20 cm^3 aliqouts of water acidified with a few drops of hydrochloric acid. The residue and disc were discarded. The filtrate was transferred to a 250 cm^3 beaker, covered with a watch glass and carefully taken to dryness on a hot plate and allowed to cool. 20 cm^3 concentrated nitric acid was added and a few crystals of potassium permanganate. The acid was boiled to dryness and the procedure repeated. After cooling the Soxhlet extract was added and the acetone removed on a boiling water bath. 5 cm^3 of bromine solution was added and retained at room temperature for 10 min with occasional stirring. 10 cm^3 concentrated nitric acid was added and the mixture stirred for 10 min and the bromine removed by evaporation on a water bath. 5 cm^3 concentrated hydrochloric acid was added and the solution taken to dryness on a hot plate. Addition of hydrochloric acid followed by evaporation was repeated twice. 10 cm^3 water was added and boiled

nearly to dryness. 10 cm^3 further water was added and boiled. After cooling, the pH of the solution was adjusted to 4-4.5 with sodium hydroxide and made to 20 cm^3. Sulphate was determined as described in Chapter 9, and represented the organic + elemental sulphur component. The level of sulphate found in a reagent blank was found to be negligible and a LOD of 100 mg kg^{-1} was indicated.

RESULTS.

The results obtained are illustrated in Table 5.20 below.

5.7.5.2. FORMS OF SULPHUR FOUND IN THE SEDIMENT.

More work is required for the comprehensive determination of the forms of sulphur present in the cores, particularly in the lower red-brown and in the grey zones. The quantity of A.V.S. occuring decreased to a negligible level in each core at between 30-60 mm above the point at which iron and total sulphur levels rose significantly. At the 60-90 mm horizon it is evident that 30-50% of the sulphur existed as sulphate while organic sulphur was negligible in core 39 but the dominant form in the other cores. Pyrite was also determined in red mud and found to be insignificant. The pyrite found in cores 14 and 45 therefore appeared to have been authigenic, but more work is needed to confirm this and to obtain a pattern for the rest of the core profiles.

Pyrite is generally considered to be one of the final stages in the diagenesis of sulphur[122], resulting from the reaction of elemental sulphur with iron(II) sulphide formed by the interaction of iron minerals [generally iron(III) oxyhydroxide] with hydrogen sulphide.

Core	segment (mm)	total Fe	total S	sulphate S	A.V.S.	pyrite S	organic S + S^{O}
14	0- 30				41		
	30- 60	10940	1108		64		
	60- 90	10100	1336	494	48	38	829
	90-12	14660	3083		67		
	120-150	17270	4934		77		
	150-180	12900	3071		62		
	180-210	15690	4208		21		
	210-240	17060	4678		14		
	240-270	23420	5720		6		
	270-300	29520	6658		8		
	300-330	34330	8519		4		
	330-360	36030	13194		5		
	360-390	40310	19667		6		
	390-420	45150	20553		4		

Core	segment (mm)	total Fe	total S	sulphate S	A.V.S.	pyrite S	organic S + S^{O}
39	0- 30	21560			33		
	30- 60	25020	1162		62		
	60- 90	25790	832	497	20	381	<100
	90-120	25730	115		14		
	120-150	25750	769		47		
	150-180	26190	1708		30		
	180-210	30640	2705		18		
	210-240	24440	2114		14		
	240-270	15680	2531		6		
	270-300	24940	7476		6		
	300-330	34650	22835		4		
	330-360	45230	40651		6		
	360-390	42070	38874		5		

Core	segment (mm)	total Fe	total S	sulphate S	A.V.S.	pyrite S	organic S + S^{O}
45	0- 30	19760			18		
	30- 60	21170	1641		18		
	60- 90	22060	1694	386	15	546	715
	90-120	24920	1809		14		
	120-150	27680	1856		6		
	150-180	29860	2520		4		
	180-210	34620	4655		7		

All results in mg S kg^{-1} dry weight of sediment.

TABLE 5.20. Results of the determination of forms of sulphur in the sediment.

Hydrogen sulphide is released by the bacterial decomposition of organic matter and sulphate (Chapter 5.7.4.1). Figure 5.27 provides a diagramatic representation of pyrite formation.

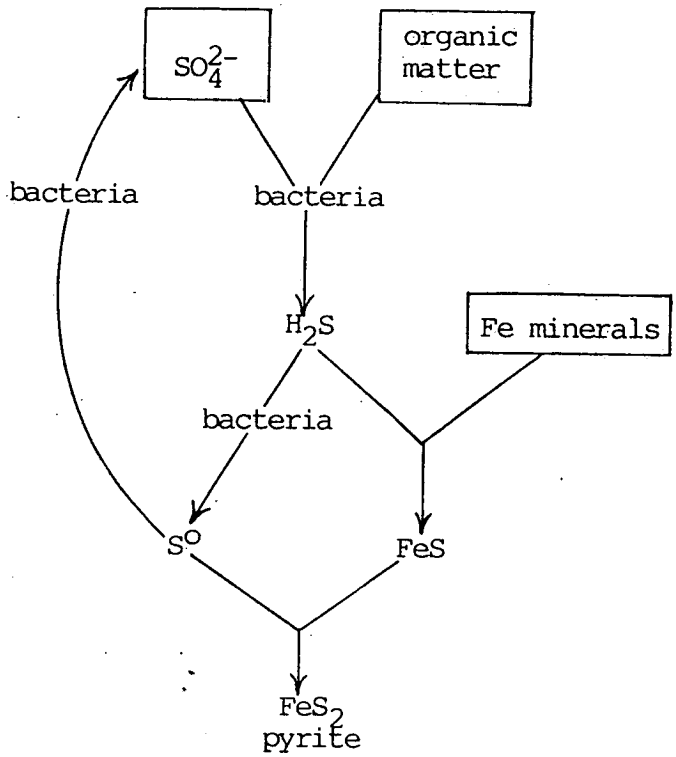


FIGURE 5.27. Diagramatic representation of the process of pyrite formation in recent sediments. (Taken from Berner[123])

Iron sulphide is readily formed due to its very low solubility[21]. Elemental sulphur is found in all sediments generally in an extremely finely dispersed state. Berner[118] considers that the amount of pyrite formed is limited by the availability of reasonably fresh organic matter. Formation is favoured by a vigorous bacterial sulphate reduction regime with a fine grained source of iron, and operates close to the mud-water interface where an adequate supply of sulphate may be assured. Such a regime requires a relatively high rate of accumulation for organic matter supply. Berner reports that most pyrite is formed in the top few cm of sediment where sulphate is

replenished by the overlying waters, and that pyrite formation becomes exceedingly slow after further burial. Pyrite formation is considered insignificant in freshwater sediment because of the limiting sulphate concentration[118,123]. In marine situations, recent sediments typically contain 0.22% pyrite[115]. Berner[115] prepared pyrite from iron(II) sulphide and sulphur at 65°C and neutral pH, but at high reagent concentrations.

Rickard[124,125] has considered the kinetics of the reactions and the rate equations he propsed have been used by Gardner[126] in constructing the following equations.

$$2FeOOH + 4H^+ + 2HS^-_{(aq)} + S^{2-}_{(aq)} \leftrightharpoons 2FeS_{(s)} + S^o_{(s)} + 4H_2O$$

where $d(FeS)/dt = K_1(H^+)^2(H_2S)^{3/2}A_g$

$$2FeS_{(s)} + S^o_{(s)} + H^+ + HS^-_{(aq)} \leftrightharpoons 2FeS_{2(s)} + H_{2(aq)}$$

where $d(FeS_2)/dt = K_2(H^+)(H_2S)A_i^2A_s$

where species in parenthesis indicate activities, K_1 and K_2 are rate constants, and A = surface area of iron oxyhydroxide (g), iron sulphide (i), and sulphur (s).

Gardner[126] considered his proposal for the equation forming pyrite to be inadequate. The problem of bringing widely dispersed FeS and sulphur into a suitable reaction environment had been considered by Rickard[125] who proposed a solubilization of elemental sulphur by polysulphide and of iron sulphide by protons. He managed to synthesise pyrite from a concentrated solution of Fe^{2+} and polysulphide, and proposed the following equation to describe the reaction occuring.

$$S_nS^{2-} + S_8 \rightleftharpoons S_{n+8}S^{2-} \text{ (etc)}$$

$$FeS + H^+ \rightleftharpoons Fe^{2+} + HS^-$$

$$Fe^{2+} + S_5S^{2-} + HS^- \rightleftharpoons FeS_2 + S_4S^{2-} + H^+ \text{ (etc)}$$

However Gardner points out that this reaction is second order for FeS and first order for sulphur and would result in stoichiometric existence of FeS and FeS_2 in sediments due to the exhaustion of elemental sulphur. Beside this spatial problem of bringing reactants together Gardner also considered that the formation of hydrogen during pyritization had not been observed. A further problem was the thermodynamic stability of FeS over FeS_2 which would suggest a very slow rate of conversion. However, the two minerals are rarely found together[126].

Howarth[127] proposed that pyrite could be formed very rapidly (within a day or less) without a FeS intermediate. He found that $^{35}SO_4$ was taken up very rapidly in the surface peat of a salt marsh with pyrite forming a major end product. Laboratory and field experiments confirmed the production of FeS and FeS_2 at pH 4 but FeS alone at higher pH. However when the partial pressure of H_2S was reduced from 1 A to 10^{-4} A, a small yeild of pyrite was the only sulphide formed. Howarth proposed that at low concentrations of HS^-, produced either by low total sulphide or by low pH (shift to H_2S at equilibrium), pyrite is formed preferentially. This will occur when the ion activity product $[(Fe^{2+})(S^{2-})]$ falls below approximately 2×10^{-18}, the solubility product of FeS, as pyrite is less soluble. Thus it is possible that in a difficult situation, with a high potential supply of iron and sulphide and a Eh regime that could support reduction at times of local pH lowering, large amounts of pyrite could be formed.

5.7.6. CORRELATION BETWEEN TRACE METALS.

For the standard comparable core segments illustrated in Figure 5.8., copper and sulphur are correlated to iron in the "native" material of segment set 2 (Table 5.17) presumably by the formation of mixed sulphide or oxide, or by similar adsorption process. No correlations exist at all for segment set 1 except that between copper and organic carbon.

5.7.6.1. COPPER AND CHROMIUM.

Figure 5.28 shows this correlation extended to take in the upper part of the cores (and including the grey zones) and shows a favourable relationship, with the exception of the grey zone of core 39 and two segments immediately above. The intercept of the correlation line passes close to the origin indicating that all the copper in the upper segments is associated with organic carbon. This behaviour has been observed previously[26,128]. Copper readily forms soluble humic complexes and these complexes appear to be independant of prevailing alkalinity or redox[34]. It is found that adsorption onto hydrous iron oxides is inhibited by this behaviour[31]. However once copper is fixed into the sediment it is not remobilized[129]. Thus copper may be distributed in a manner related to soluble organic matter and be fixed once the material has been coagulated or precipitated by some other process.

Chromium follows a similar pattern to copper as indicated in Figure 5.29, although the association is not as good, particularly in core 39. Most of the total copper entering the loch arrived with the leachate (0.33 mg l^{-1}) rather than the north inlet (<0.0001 mg l^{-1}), depositing 17 mg kg^{-1} in the sediment. The observed range for the

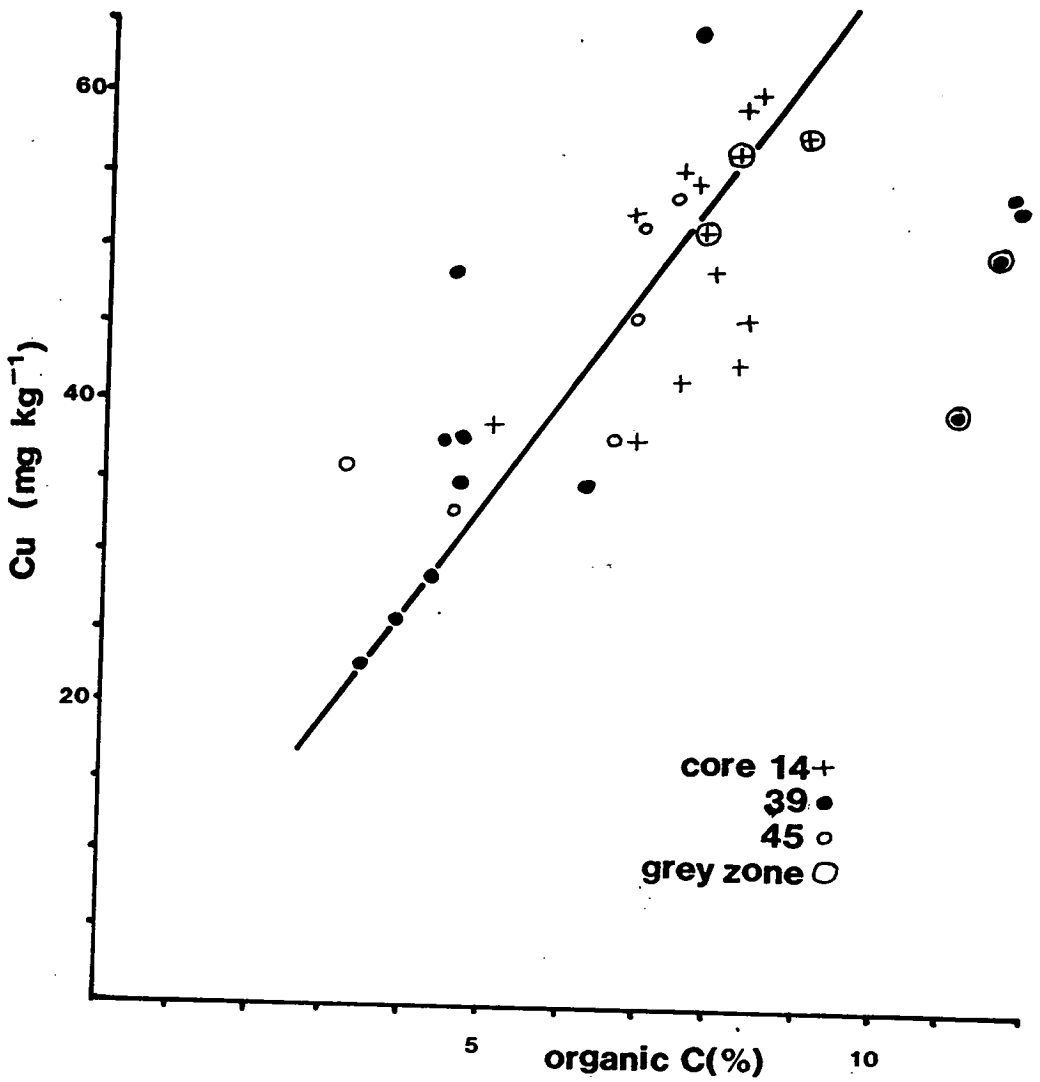


FIGURE 5.28. Correlation of copper and organic carbon in the upper parts of the cores.

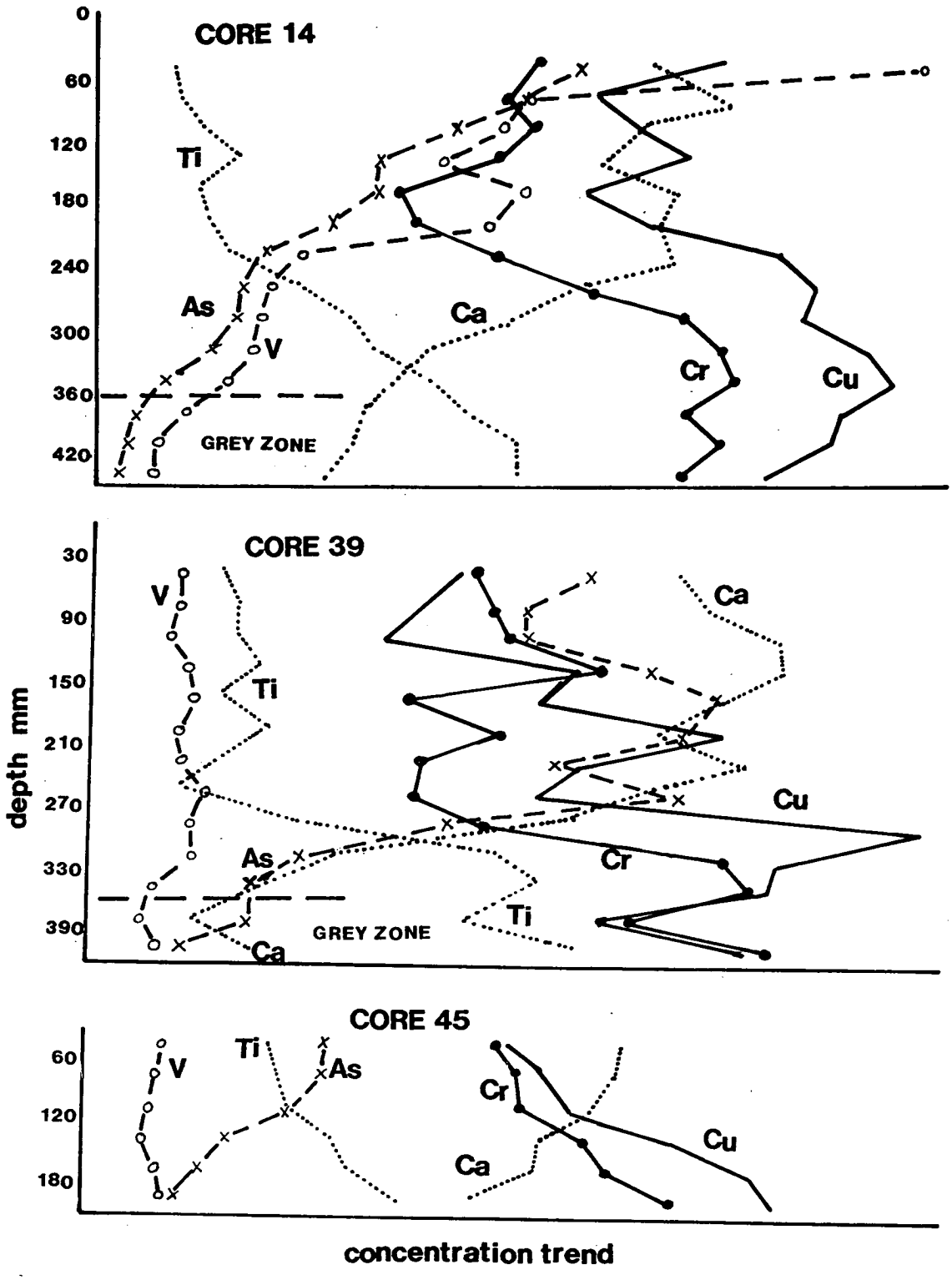


FIGURE 5.29. Concentration of related trace elements relative to calcium and titanium.

top of the sediment of 23 mg kg^{-1} for core 39 to 49 mg kg^{-1} for core 14 probably reflects an additional atmospheric supply. Cawse[59] gave a range for atmospheric input representing 5-11 mg kg^{-1} in the sediment. Input of total chromium was again mainly from the leachate (0.1 mg l^{-1}) rather than the north inlet (<0.0001 mg l^{-1}), giving 53 mg kg^{-1} in the sediment. Even allowing for an atmospheric input of 0.6-4 mg kg^{-1} a large deficiency is evident compared with the 120-137 mg kg^{-1} found in the top part of the sediment. Although Figure 5.29 may indicate a slight tendency to surficial enrichment of chromium relative to copper this is inadequate to explain the discrepancy. Chromium, unlike copper, is readily soluble at leachate pH and additional supplies of chromium may arrive as slugs of dissolved chromium at times, due to particular characteristics of bauxite batches, red mud or factory practices. This mode of supply has not been investigated. Thus chromium and copper appear to be related to organic carbon content and are not noticeably surficially enriched in the sediments.

5.7.6.2 NICKEL, LEAD, AND ZINC.

Figure 5.30 indicates that the origin of these metals was from detrital input (plus an atmospheric component) and that they have proved to be basically immobile in the sediment. Nickel supply to the sediment from known detrital sources was 31 mg kg^{-1} with a possible 4-11 mg kg^{-1} by atmospheric input[59], while levels found in the top of the sediment varied from 35 mg kg^{-1} to a high of 71 mg kg^{-1} for station 45. It is probable that detritus entering through the north inlet will have provided this high level at station 45. Zinc supply shows a detrital correlation with titanium in cores 14 and 39. The supply to the sediment was 46 mg kg^{-1} from detrital inputs plus a

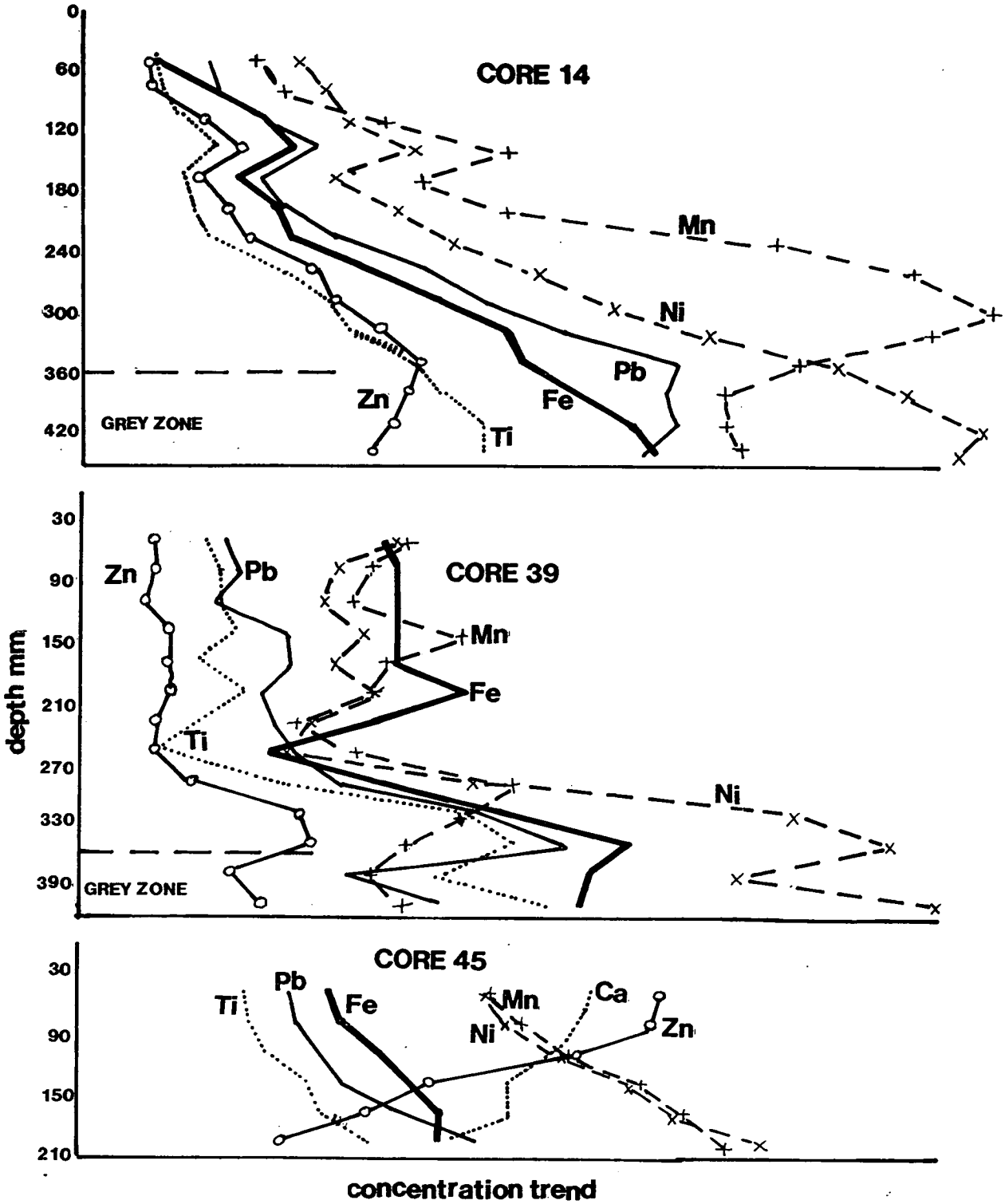


FIGURE 5.30. Concentration of related trace elements relative to titanium and iron

possible 27-107 mg kg^{-1} from the atmosphere. Levels found for these two cores were 52 and 53 mg kg^{-1} respectively. The level recorded in core 45 was 384 mg kg^{-1} with a spatial variation inversely correlated with detrital input. Zinc was not correlated with silica which would have indicated ion-exchange active aluminosilicates (Chapter 5.7.3). The only possible correlation would be with calcium (as shown in the figure) with the co-precipitation of zinc carbonate on calcite. The ion radius of Zn^{2+} (0.74 Å) is similar to other ions which form solid solutions with calcite such as Fe^{2+} (0.76 Å) and Mn^{2+} (0.80 Å) compared to Ca^{2+} at 0.99 Å (see Chapter 5.7.2). Zinc is greatly surficially enriched and a mechanism of re-solution of carbonates followed by deposition at higher pH and Eh* near the sediment surface would need to be proposed. It would appear from Chapter 5.5 that at station 35, which is situated 50 m south of station 45, active re-solution of calcium was occuring in the core (rising to 87 mg l^{-1} in the interstitial water at 60-90 mm depth). The process appeared to be unrelated to sulphate and probably represented active methane production.

5.7.6.3. MANGANESE.

Manganese follows a similar pattern to iron in the sediment profiles (Figure 5.30), but substantial maxima occur in cores 14 and 39 at a depth immediately below the point at which acid volatile sulphide (A.V.S.) disappears and before total sulphur levels became very high (this rise is not significant in core 45). This relationship is illustrated in Figure 5.31. Interestingly A.V.S. forms maxima at the same position as the more abundant manganese forms minor maxima, and suggests that A.V.S. may well comprise MnS rather than FeS, a

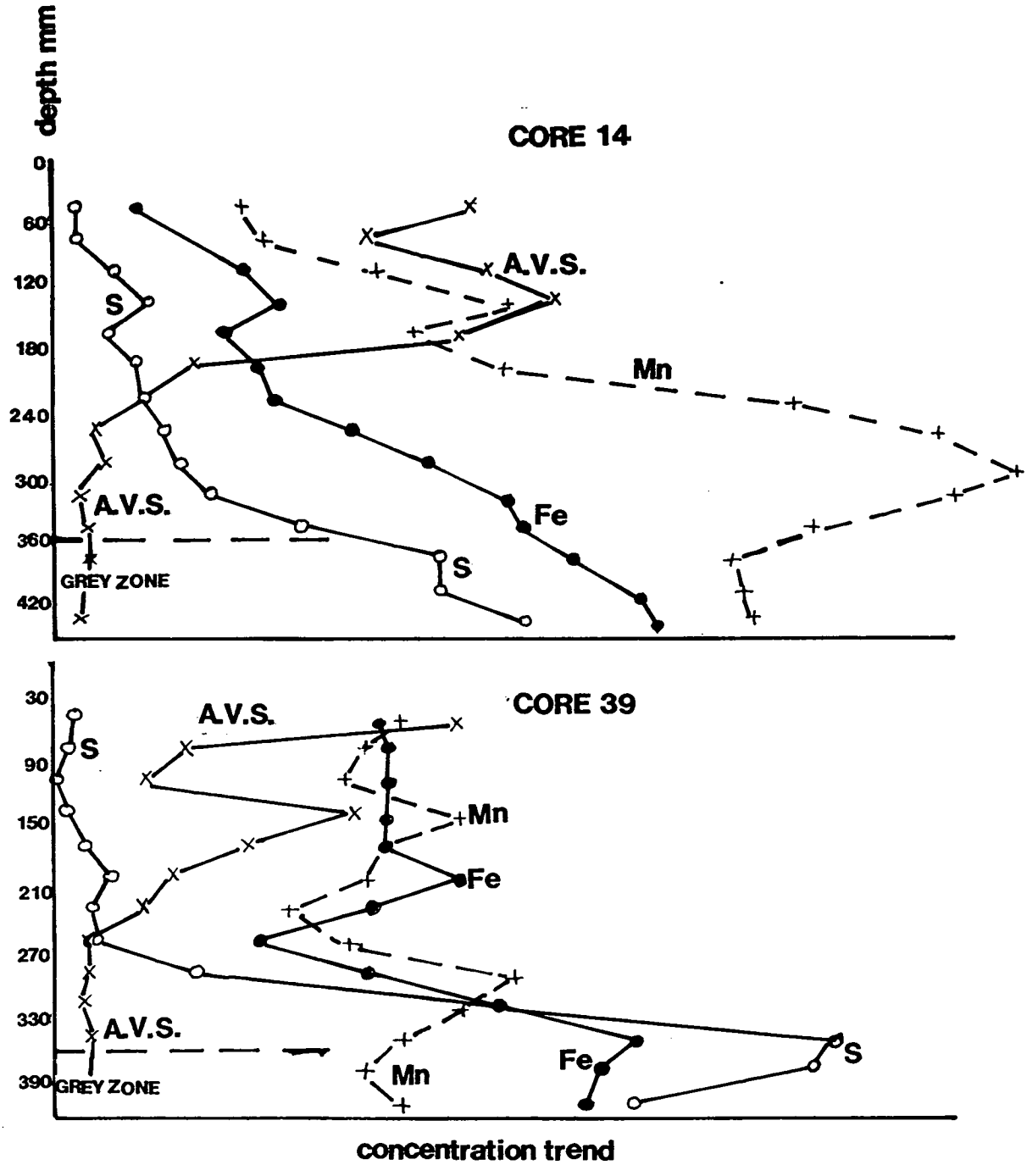


FIGURE 5.31 Relative concentrations of iron, manganese and sulphur in the upper parts of the cores.

reductive process which would occur at a higher Eh value at high pH. If the following reactions are considered:

$$FeOOH_{(c)} + SO_{4(aq)}^{2-} + 11H^{+} + 9e \rightleftharpoons FeS_{(c)} + 6H_2O$$

$$MnOOH_{(c)} + SO_{4(aq)}^{2-} + 11H^{+} + 9e \rightleftharpoons MnS_{(c)} + 6H_2O$$

$$MnO_{2(c)} + SO_{4(aq)}^{2-} + 12H^{+} + 10e \rightleftharpoons MnS_{(c)} + 6H_2O$$

then $Eh_{FeS(FeOOH)} = 338 + 6.2871\log(SO_4^{2-}) - 69.16pH$ (in mV)

and $Eh_{MnS(MnOOH)} = 390 + 6.2871\log(SO_4^{2-}) - 69.16pH$

and $Eh_{MnS(MnO2)} = 459 + 5.92\log(SO_4^{2-}) - 71pH$

Thus MnS may form at a Eh value at least 52 mV above that for FeS or for a pH of 0.75 units more alkaline.

Manganese is massively enriched in the sediment. The inputs to the sediment represents 28 mg kg^{-1} with <4-17 mg kg^{-} of possible atmospheric input[59]. However levels found at 30-60 mm in the sediment ranged from 278 mg kg^{-1} to 676 mg kg^{-1} (at station 45). Manganese is readily transported in sediments under reducing conditions and the most probable source of this material would be from the naturally occuring levels in the "natural" sediments. Levels in natural lake sediments vary widely with a mean of 2% being found in Lake Windermere for surface sediments for an iron content of 5% (Rowlatt[11]), while in Lake Michigan surface levels of 590 mg kg^{-1} were reported, associated with an iron content of 2.8%. Macrophytes and leaves, of which much of the "natural" sediment will have been composed, contains considerable manganese[130] (up to 4000 mg kg^{-1}) relative to iron at 100 mg kg^{-1}.

The profile of manganese for cores 14 and 45 show a steady gradient from the grey zone (or "natural" zone for core 45) to the surface

indicative of the concentration gradient that would be expected to permeate the interstitial water. This gradient in the interstitial water has been observed by Sakata[129] who concluded it was due to solution processes involving the formation of hydrous ferro-manganese oxides. He concluded that the formation of sulphide minerals was not involved. Mn^{2+} may also be mobilised by the formation of $MnCO_3$, $Mn_3(PO_4)_3.8H_2O$, or MnS at transient high Mn^{2+} levels followed by re-solution as the concentration in solution decreases. However alabandite (MnS) is relatively soluble and the solubility product of log K = -15.7 for $(Mn^{2+})(S^{2-})$ may not easily be exceeded[131]. Thus the band of MnS that apparently found may be continually redissolved and redeposited as Mn^{2+} progresses upwards and be defined solely in terms of S^{2-} availability. Two peaks disrupt this gradient, one being the A.V.S. mineralisation band and the other being the deposition band immediately above the grey zone. This bond may represent a substantial sink of MnS if sulphide is continually leached from the organic sulphur/pyrite band below.

5.7.6.4. VANADIUM AND ARSENIC.

Arsenic and vanadium are supplied entirely from the leachate and the level of supply will be related to the volume of leachate entering at any one time. Both elements are seen to be related to sediment calcium in core 14 (Figure 5.29), as would be expected since calcium supply is determined by leachate supply of carbonate. Although arsenic remains correlated to calcium in the other cores, vanadium incorporation remains constant.

Several workers (e.g. Faust et al[46]) have found that no matter what species are prevalent in the water body, As^{5+} predominates in the

interstitial water, making up some 80% of the arsenic present. The level in the interstitial water may be thousands of times higher than in the water body and forms a permanent reservoir for arsenic replenishment of the water body. It is thought that arsenic exists in the sediment mainly as $FeAsO_4$ or $FeAs_2$ (Faust et al[46]). The order of dominance in interstitial water has been found to be As^{5+}> As^{3+}> MMAA> DMAA, and this should be compared with that found in the loch body under Chapter 4.7.6. Arsenic levels in interstitial water is reported to be strongly correlated with Fe^{2+} (Brooks et al[132], Lemmo et al[48]) although this is not clearly indicated with the present analysis displayed in Tables 5.18 and 5.19. Total arsenic is not correlated with iron, sulphur, organic carbon or phosphorus in the cores. Hydrogen sulphide may react with arsenic liberated to the interstitial water to form metallic mixed sulphide-arsenides or polymeric organoarsenicals containing sulphur[48]. At depth under severely reducing conditions arsine may be formed abiotically or else methylated arsines by biotic reaction[48]. Either process would result in a loss of arsine to the atmosphere as these gases are not very soluble. Also it was stated in Chapter 4.7.6 that phytoplankton may provide highly reducing microenvironments which yeild trimethyl arsine to the atmosphere from the water body. Figure 5.32 illustrates the very rapid drop in the concentration of arsenic within the core and must represent a loss, either into the water column or to atmosphere. The figure indicates a similar reduction in vanadium which is considered to indicate a historically slightly lower input of vanadium combined with perhaps an equal amount being retained at the sediment surface by oxidation-reduction processes. The loss of arsenic is more pronounced and although this will indicate a slight reduction in input historically (As and V are correlated in the loch water) it

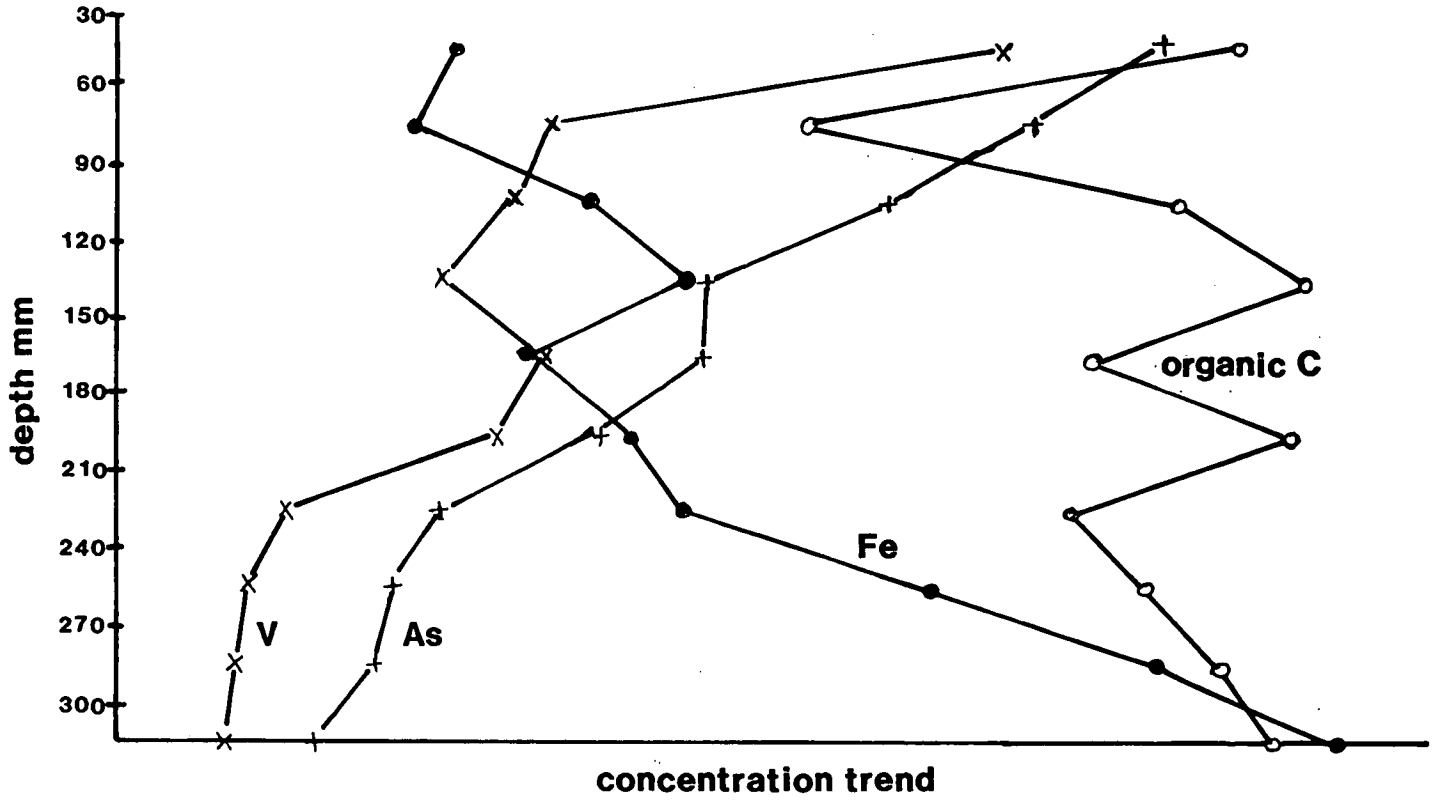


FIGURE 5.32. Relative concentration of arsenic and related elements in the upper part of core 14.

probably represents a considerable level of volatile loss both from the sediment and from phytoplankton within the loch body. This concentration of arsenic in the uppermost parts of the sediment is well known and controlled by reduction-oxidation processes (e.g. Holm et al[52]).

In Chapter 5.7.5 it was indicated that Fe(III) must be present throughout the upper parts of the cores and it is probable that arsenic is held in steady state with this by a redox reaction such that[133]:

$$3Fe(OH)_3 + HAsO_2 + H^+ \rightleftharpoons 2Fe^{2+} + FeAsO_4 + 4H_2O$$

Such a reaction will control the speciation of As(V) and As(III) and probably means that much of the arsenic remains as $HAsO_4^{2-}$, $FeAsO_4$, and arsenious oxide (As_2O_3) all of which are viable at pH 10 over the range of Eh values found in the cores[48]. Thus a complex situation is evident with oxidised states apparently co-existing with biotically generated methylated arsines.

It is probable that some of the arsenic input to the loch never reached the sediment but was gassed out via the phytoplankton. The reduction of ferric surfaces on which sorption had occurred will have released arsenic into the interstitial water and most of this material will have been resorbed by precipitating iron oxyhydroxides at the surface, thus giving permanent surface enhancement. As(III) species will however be less likely than As(V) to be retrapped and may be released to the water body. Evidence from Chapter 4.7.6. suggests that arsenic undergoes regular biotic involvement and this cycle of oxidation and reduction processes renders arsenic very mobile with the end product being expelled to atmosphere.

Core 45 provides a non-enriched assimilation of arsenic (384 mg kg^{-1} against 400 mg kg^{-1} projected supply) while core 39 shows a 50% enhancement throughout, as would be expected at this station, but no indication of surficial enrichment. Core 14 indicates significant surficial enrichment of arsenic and will represent redistribution caused by oxidation reduction processes undergone by the iron oxyhydroxide substrate on which arsenic was most likely to have been sorbed (see Chapter 5.7.6.2.).

Vanadium occurs at a relatively constant level in cores 39 and 45 despite the increased supply in recent years. Core 14, on the other hand shows considerable (5 times) enrichment in the top 150 mm of sediment. Vanadium is strongly adsorbed by humic material and at station 14, the sedimentation of degraded organic matter will also have greatly increased in recent years. Thus it would appear that this enrichment may be the sum of two processes, firstly the excess deposition by humic matter and secondly a re-solution of material by reductive processes, putting solubilized humic matter, with associated vanadium, to the interface where it is then re-coagulated. This process of humic solubilization has been reported by Wetzel[21] (see also Chapter 5.7.4.1). If sedimentation by humic material is indeed responsible for vanadium deposition then significant levels of vanadium will not be deposited at station 39. Very shallow water and high pH prevent autochthonous phytoplankton deposition and the leachate provided a very low detrital input of humic material. Figure 5.23 shows that station 45 received a relatively fresh organic debris falling through a shallow depth of water (4 m as opposed to 12.8 m at station 14) which would restrict uptake of vanadium. Similarly if the body of the loch provided an efficient scavenging

medium for vanadium then the metal may not have been available at station 45 for deposition.

CHAPTER SIX

MATHEMATICAL PREDICTION OF CHEMICAL SPECIATION AND MINERAL DEPOSITION

6.1. CHOICE OF APPROPRIATE BASIS FOR MODEL.

Several models exist for the prediction of speciation of inorganic elements in water. All those investigated operate on the basis of thermodynamic equilibrium, without the introduction of meaningful kinetic bias. Drever[77] considered those of geochemical interest to include the WATEQ family based on the work of Truesdell and Jones[10] which created a large matrix of simultaneous equations containing one for each equilibrium constant and a series of mass balance equations, one for each component. WATSPEC, created by Wigley[134] operated a series of progressive incrementatal approximations on each of a similar set of equations without the creation of a specific matrix. These programs omitted the formation of minerals, being satisfied with defining whether a particular mineral was under- or over-saturated with respect to the solution.

Typical equilibrium equations were

$$\log(K_{CaHCO3+}) = \log(a_{CaHCO3+}) - \log(a_{Ca++}) - \log(a_{HCO3-})$$

and mass balance equations were of the type

$$M_{Ca(total)} = M_{Ca++} + M_{CaHCO3+} + M_{CaCO3} + M_{CaSO4} + \cdots\cdots$$

All programs used Debye-Huckel theory for the prediction of activity coefficients.

Nordstrom et al[135] compared available programs by defining speciation in typical standard waters. It was found that general agreement occurred at major element level but that considerable discrepancy was found for the speciation of trace metals. The model can only be as good as the thermodynamic data used, and much data, from different

sources is of variable accuracy. It is therefore not surprising that considerable deviations were found for some poorly understood trace metal interactions. Because of the great sensitivity of iron and manganese to redox conditions, the differing definitions of pe led to serious differences between models. For instance for a standard water, two variations on WATEQ predicted -log(M) of Fe^{2+} of 12.167 and 6.579 while MINEQL gave 15.18 and WATSPEC 11.953.

Several programs attempt to define the degree of mineral deposition or dissolution. PATHI (Helgeson *et al*[136]) allows incremental solution or deposition of minerals to bring all the solid mineral phases into equilibrium. MINEQL (Westall *et al*[137]) performs similarly except that minerals are placed in classes, some being allowed to deposit and dissolve while others being allowed formation only. The major drawback of these programs was that the incremental process of dissolution or deposition required respeciation between increments. The process generated extended running times.

Limitations were placed on the computing facilities available within the F.R.P.B. for development of the model. In its usual "multi-user" mode only BASIC programs could be run alongside others and the processing core was limited to 12K bytes. Because of the size limitations a non-matrix program was required and WATSPEC was chosen. For a full description of WATSPEC reference should be made to Wigley[134]. The model was translated from FORTRAN into single precision BASIC. This placed various limitations on the programming and instances involving the subtraction of large, similar numbers, and the progressive manipulation of successive approximations had to be replaced by other processes. If, under any circumstances

particular calculations were in doubt with regard to precision, the same calculations were performed in ALGOL to an equivalent of 10x BASIC precision. The final processes chosen were found to be in good agreement in the two languages, for instance, alkalinity recalculation for open or closed systems was found to be better than 0.001%.

6.2. RECALCULATION OF INSTANTANEOUS pH AND ALKALINITY.

The program developed as an extended system, with a WATSPEC core, and was called WATDEPOSIT. The program provided a two-water input (i.e. leachate and north inlet) for generating an instantaneous loch water "mix". WATDEPOSIT could take any number of test flow ratios, either as incremental ranges, or individual situations. It required the mixed water temperature and dissolved oxygen to be defined by the user. Each water was speciated by the WATSPEC core and these species instantaneously conserved to provide an instantaneous pH. The instantaneous pH and alkalinity was determined using the equations derived by Wigley and Plummer[138] for both atmospherically open and closed systems.

(1) Closed to the atmosphere.

The following conditions may be identified:

(i) Total inorganic carbon and alkalinity are conserved

(ii) H_2CO_3 is not conserved.

considering $C = m_{CO3--} + m_{HCO3-} + m_{H2CO3}$ (part of total C system)

and $A = 2m_{CO3--} + m_{HCO3-}$ (part of alkalinity system)

and $m_{H2CO3} = K(m_{HCO3-})^2/(m_{CO3--})$

where $K = K_{H2CO3}(\gamma_{HCO3-})^2/(K_{HCO3-}\gamma_{CO3--}\gamma_{H2CO3})$

then $m_{HCO3-} = A - 2m_{CO3--}$

$$C = m_{CO3--} + (A - 2m_{CO3--}) + K(A - 2m_{CO3--})^2/m_{CO3--}$$

and $(m_{CO3--})^2 = [m_{CO3--}(A - C - 4K) + KA^2]/(1-4K)$

Thus an iterative procedure may be applied for n number of iterations:

$$(m_{CO3--})_n = \sqrt{[(m_{CO3--})_{n-1}(A - C - 4K) + KA^2]/(1 - 4K)}$$

A satisfactory limit to be applied to the iteration was considered to be $(m_{CO3--})_n - (m_{CO3--})_{n-1} < Ax10^{-5}$.

then $m_{HCO3-} = A - 2m_{CO3--}$

$$m_{H2CO3} = K(m_{HCO3-})^2/m_{CO3--}$$

and $pH = -\log[m_{HCO3-}\,\gamma_{HCO3-}/(K_{HCO3-}\,\gamma_{H+}\,\gamma_{CO3--}m_{CO3--})]$

(2) Open to the atmosphere.

The following conditions may be identified:

(i) Alkalinity and m_{H2CO3} are conserved

(ii) Total carbon is variable.

Then $A = 2m_{CO3--} + m_{HCO3-}$

and $m_{CO3--} = K(m_{HCO3-})^2/m_{H2CO3}$

so $A = 2K(m_{HCO3-})^2/m_{H2CO3} + m_{HCO3-}$

and the iteration procedure may be applied to:

$$(m_{HCO3-})_n = \sqrt{[A - (m_{HCO3-})_{n-1}]m_{H2CO3}/2K}$$

so $m_{CO3--} = (A - m_{HCO3-})/2$

and $pH = -\log[m_{HCO3-}\,\gamma_{HCO3-}/(K_{HCO3-}\,\gamma_{H+}\,\gamma_{CO3--}m_{CO3--})]$

Programs were prepared on the basis of these equations and, using the data generated by WATDEPOSIT for the instantaneous mix, the instantaneous pH and alkalinity were calculated for equilibrium conditions

for the system both open and closed to the atmosphere. Table 6.1 illustrates the findings.

system :	closed	open
determinand:		
part total inorg. carbon (defined as C)	4.964E-3	6.997E-3
carbonate (*)	2.231E-3	2.263E-4
bicarbonate (*)	3.238E-3	7.247E-3
carbonic acid	5.990E-7	1.477E-5
pPCO2	4.9	3.5
pH	10.04	8.7

TABLE 6.1. Equilibrium conditions for a 1:7.71 mix of leachate:north inlet for systems open (pPCO2 defined as 3.5) and closed to the atmosphere. (*) indicates total of all species incorporating this ion.

The actual loch pH as observed after mixing in approximately this ratio is known to be in excess of pH 10. It is therefore evident that a CO_2 deficiency, exhibited by the leachate, persisted throughout the loch and, despite the long residence times, substantial carbon dioxide is not abstracted from the atmosphere. With this conclusion in mind it was decided to incorporate only the closed system calculation into WATDEPOSIT.

pH and alkalinity recalculation was required for the instantaneous mix of the waters and after each adjustment of mineral deposition or dissolution.

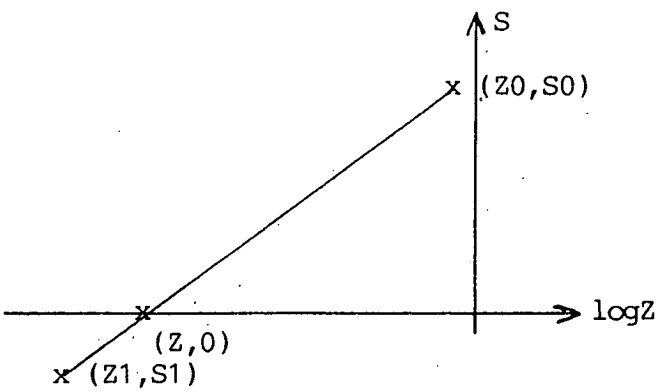
6.3. MINERAL DISSOLUTION AND DEPOSITION.

Initially an incremental technique was used for determining the correct degree of deposition of minerals to achieve equilibrium but the processing time was several hours. Consequently a technique was devised whereby using the degree of oversaturation as a guide the

total concentration of affected determinands (e.g. calcium and alkalinity) were reduced to generate a second pair of data of total concentration (Z) and saturation index (S). The saturation index was defined according to Wigley[134] by

$$S = \log[(\text{ion association product})/(\text{solubility product})]$$

Then for a first order deposition the equilibrium concentration was achieved according to the diagram below



where for initial data pair (Z0,S0), and over-deposition pair (Z1,S1), the equilibrium pair (Z,0) is determined by

$$\log(Z) = S1[\log(Z1)-\log(Z0)]/(S0-S1) + \log(Z1)$$

and the amount of determinand to be redissolved (G) for N mol of determinand for each mol of mineral was

$$G = Z1 \times 10^{\{S1[\log(Z1)-\log(Z0)]\}/[(S0-S1)-1]/N}$$

For determinands with higher orders of relationship to the mineral this treatment becomes approximate but it was found that two iterations of this calcultion almost always brought the saturation to within 10% (± 0.01 units on S). Where more than one related mineral may form they are deposited in pairs. Over- and under-saturation concentrations/saturation index data pairs were generated for

equilibrium of the second mineral (e.g. for calcite and dolomite) and the equilibrium position generated for that mineral. This treatment generally retained the second mineral within the limits specified for equilibrium. If this did not occur then two passes through the routine nearly always generated mutual equilibrium.

6.4. SPECIFIED MINERALS.

Initial runs of the model produced unrealistic results. As calcium aluminosilicates were more insoluble than calcite they precipitated in abundance until aluminium and silicon levels were reduced to near zero. Since this is known not to occur because of kinetic considerations, it was decided to attempt to incorporate kinetic data or at least a degree of diffusion control. Kinetic data for aluminosilicate mineral formation proved to be extremely sparse, and represents an area of research that has been neglected. Some data on the dissolution of rock-forming minerals is available but would be of little use in this context. Kinetics concerning the formation of calcite and dolomite are found to be the subject of controversy (see Chapter 4.7.1 and for dolomite consult Shimmield[26] and others).

Thus it was eventually decided to abandon this approach and apply the system of classes applied arbitrarily by others (e.g. Westall et al[137]). A series of base minerals were determined as Key minerals, and as far as the work progressed, the deposition of aluminosilicates was not assessed. Again this gave unreliable results. Appendix F contains final printouts for a 1:7.71 mix of leachate to inlet water allowed to equilibrate to calcite and dolomite production. The printouts incude initial speciation of leachate and inlet water prior to mixing. Included is a calculation of run time and central

processor unit time. It will be seen that eventually some eight times as much dolomite was formed compared to calcite. Dolomite is known to form very slowly, whereas calcite formation is rapid. Dolomite is not found in the loch. Thus it must be concluded that this approach to the modelling leaves much to be desired and until a proper kinetic basis, with a thorough understanding and allowance for interferences (e.g. sulphate on dolomite), is available, the value of making allowance for dissolution/deposition must be in question.

Further limitations that were not considered by the model were

(1) the influence of dissolved organic matter

(2) the influence of phytoplanktonic activity

(3) uneven mixing within the loch

(4) redox reactions at the mud-water interface

More elaborate models, involving the integration of several disciplines into the effects being modelled, are currently developing and reference should be made to Orlob[139] for some indication of the current state of the art in the field of water quality modeling.

6.5. THE MODEL.

The program comprises WATDEPOSIT which inputs all relevant data and calculates all activity coefficients, and equilibrium and association constants which are written to file. ITERATE is chained which speciates the leachate and north inlet waters and then calculates an instantaneous pH and total determinands for the mixture being tested. The mixture is speciated and tested for supersaturation of key minerals, when the necessary adjustments are made to determinand concentrations so as to leave all key minerals in equilibrium.

Appendix E.4 lists these programs.

It was originally intended to add determinands to the model which were of special interest in Kinghorn Loch. These included phosphorus, arsenic, vanadium, and fluorine. Additional information is available for a large number of extra aluminosilicate and other minerals which would have been relevant. However, due to the limitations in uses for the model that are apparent, this was not done. Suitable data for carrying out this work was found in Drever[77], Truesdell and Jones[10], Smith and Martell[140], Nriagu[141], Ball et al[142] and Ball et al[143].

6.6. APPLICATION.

The model, despite its considerable inherent limitations, proved extremely useful in determining starter pH's for several experiments and in finding limiting levels of determinands so as to prevent the deposition of minerals, primarily calcite, in several experiments (achieved by the interuption of the mineral deposition sequences at an appropriate stage). It also served to illustrate the difficulties involved in attempting to allow for mineral formation and dissolution.

CHAPTER SEVEN

ASSESSMENT OF BIOLOGICAL ACTIVITY

7.1. BENTHIC INVERTEBRATES

7.1.1. SAMPLING TECHNIQUES.

Benthic invertebrates existed throughout the loch but were most abundant in the littoral margins. These areas provided protection against the worst excesses of the pollution load and a source of detrital food. However, because of the variability of littoral environment, any meaningful appraisal of populations is extremely difficult to obtain. It was the aim of this chapter to use a statistical process to follow the recovery of the invertebrate population after 1983. This could only be done by considering the non-littoral stations within the loch. Forty two such stations, situated on mud or gravel, were identified and this was considered to be a satisfactory number for quantitative analysis (Drake[65]). In the event, further decline after 1981 and subsequent recovery after May 1983 was so marked that such an appraisal was not considered necessary.

A small Van-Veen grab (Figure 5.1) was used which gave a "bite" of 0.025 m^2. Since the surface of the sediment sample obtained was generally within 5-10 mm of the doors of the grab it was considered that the recovery of invertebrates dwelling within the area sampled will have been good.

During 1981, three surveys were undertaken during the year in order to identify a period when animal size and abundance was optimum for quantitative determination. It was intended to undertake seasonal surveys but due to severe weather the winter and spring dates were combined as the loch surface remained frozen until the end of February. As expected, Spring proved most suitable and further surveys were undertaken during Spring of 1982-1984. Samples were

taken from as many of the 51 stations as were accessible. On lifting the grab, the sample was transferred to a heavy duty polythene bag and 50 cm^3 40% formaldehyde solution added. The bag was securely tied and the contents thoroughly worked with the hands to ensure full penetration of formaldehyde. The bags were stored at 4^oC and prepared within 7 days. On removal from storage the sample was transferred in small lots to a 250 um sieve, a gentle jet of water being used to wash the mud through the sieve. When all the sample had been added the water action was continued for some time until the water passing the sieve was clear. The residue was carefully and completely transferred to a white basin where all organisms were separated and transferred to 25 cm^3 specimen jars with snap-on tops. The jars contained 95% ethanol in water with 5% glycerol added. The jars were stored for later analysis (performed November 1984-February 1985). Brinkhurst[144] stated that a 250 um sieve should be used for separation, as the number of organisms recovered could be increased by 600% when going from 1 mm to 250 um sieve, and that chironomids several mm in length could be lost. It was evident that many organisms, principally in the littoral areas, were indeed very small.

7.1.2. IDENTIFICATION.

Identification was achieved by initial separation of Chironomus Sp. and Glyptotendipes Sp. from the remainder. All the individuals from the remaining fauna were mounted after decapitation and the slides allowed to clear before identification was attempted. A large number of individuals of Chironomus Sp. and Glyptotendipes Sp. were also mounted for confirmatory analysis. Identification to genus was achieved by microscopic examination according to the keys set out in Table 7.1. I.Fozzard, in pursuence of his duties with the F.R.P.B.,

had raised larvae from the loch to the adult stage. This allowed him to identify several of the fauna to species level. By association with his findings, invertebrates obtained during the present study were tentatively identified to species level. Table 7.2 sets out a list of these fauna.

I should like to express my appreciation to I.Fozzard for explaining the finer points of the anatomy of these individuals with reference to the Keys.

7.1.3. ENVIRONMENTAL REQUIREMENTS OF FAUNAL TYPES.

It is generally considered that the most tolerant of the benthic organisms, occuring in greater numbers than anything else in polluted systems, are tubificid worms. Their occurence is considered diagnostically very useful in conditions too limiting for chironomids[144]. Slepukhina[152] reported that in heavily (organically) polluted areas of North Caucasus, oligochaetes formed up to 80% of the faunal mass and occurred at densities of 6000-8000 m^{-2}. In some pools this abundance dropped to 30% with C.plumosus becoming abundant. However, these worms did not occur at all in the non-littoral sediments of Kinghorn Loch and are not very abundant even in the littoral margins. Thus, toxic effects other than low dissolved oxygen, must have discouraged their development. Oligochaetes in general are known to be sensitive to heavy metal pollution and their absence may be used as an indicator of toxic materials[152]. This effect is evidently occuring in Kinghorn Loch.

Family	genus	key	figure/page no.
Chironomidae	Chironomus	Pinder and Reiss[145]	Fig.10.6
	Glyptotendipes	-.-	10.29
	Microtendipes	-.-	10.43
	Brillia	Cranston[146]	16
	Procladius	Fittkau and Roback[147]	5.27
	Arctopelopia	-.-	5.5
Culicidae	Chaoborus		
Limnephilidae	Limnephilus	Hickin[148]	531-535
Sialidae	Sialis	Elliott[149]	12
Corixidae	Sigara	Macan[150]	45
Enchytraeidae		Brinkhurst[151]	Page 12,44
Tubificidae		-.-	12,29
Lumbricidae	Eiseniella	-.-	13,51

TABLE 7.1. Keys used in the identification to Family or Genus.

subfamily	tribe	genus	species (tentative)
(midges:)			
Chironomidae	Chironomini	Chironomus	plumosus
		Glyptotendipes	barbipes
		Microtendipes	(pedellus gp.)
Orthocladiinae	Orthocladiini	Brillia	modesta
		Cricotopus	
Tanypodinae	Macropelopiini	Procladius	(sagittalis)
		Macropelopia	
	Pentaneurini	Arctopelopia	
Culicidae		Chaoborus	(flavicans)
(water bug:)		Sigara	concinna
(alderfly:)		Sialis	lutaria
(caddis fly:)		Limnephilus	flavicornis
(worms:)			
Lumbricidae		Eiseniella	tetraedra
Tubificidae			
Enchytraeidae			

TABLE 7.2. List of benthic fauna found during the period of study.

Chironomus plumosus is known to be extremely abundant in highly eutrophic lakes under conditions of low dissolved oxygen[144]. Certain red-blooded chironomids, notably C.plumosus, can thrive in septic conditions and it is considered by Gaufin[153] that the haemoglobin in

the blood acts for both transport and storage of oxygen passing through the cuticle, thereby allowing a continuance of filter feeding even under sustained anaerobic conditions. Thus certain Chironomus species are well adapted to extremely low tensions of dissolved oxygen. Lueschow[53], in his study of lakes (in Pewaukee, Wisconsin) that had been treated over many years with arsenite, found that C.plumosus occurred in numbers up to 2500 m^{-2} within lake sediments containing up to 1900 mg As kg^{-1}. He also found that Chaoborus punctipennis (an American species) occurred under similar conditions, but that other invertebrates were absent. This author identified C.plumosus, but it is only relatively recently that the common practise of terming any Chironomus with ventral tubules as plumosus has been superceded by more discerning terminology.

Glyptotendipes barbipes is not able to operate in such low oxygen conditions and occurred in the old littoral and sub-littoral areas of the loch. This species is common in brackish water in lowland England and is tolerant of more saline waters than any other species in the genus[154]. Microtendipes Sp. is very common in pools containing soft sediment throughout the F.R.P.B. area, but is generally considered to be intolerant of polluted conditions and brackish water. Thus it is surprising that it colonized the loch at a time of greatest stress.

Chaoborus is not a benthic invertebrate. It is a carnivor that feeds on the zooplankton by night and retreats to the mud surface during the day. It was found to occur in the deeper parts of the loch where Chironomus plumosus was absent. Brinkhurst[144] considers that Chaoborus is more able to thrive under conditions of extreme stress.

7.1.4. SUMMARY OF F.R.P.B. SURVEYS.

Each of these surveys were carried out by I.Fozzard and the Biology Section of the F.R.P.B., Stirling office. A survey carried out during July 1976 indicated that the biota was very restricted although Sphaerium Sp. (freshwater cockle) and ostracods (minute crustacea) were common at the time. Caddis flies and mayflies were absent. The only common macrophyte was Polygonum amphibium. Chironomids, Chaoborus (phantom midge) and Sigara concinna were also found. Although Oscillatoria ("blue-green algae") was mentioned in the report it is not known whether it occured as an extensive bloom or just on the P.amphibium.

By June 1979 growth of P.amphibium had become restricted in several areas. Octracoda was reported in the north west corner of the loch although Sphaerium Sp. was not. Chironomus Sp., Procladius Sp., and Chaoborus Sp. were reported from the grab samples while Sigara concinna and Glyptotendipes Sp. were only reported from sweep samples (along with eight other chironomid species). The development of zooplankton was found to be extremely limited.

The survey carried out in July 1984 provided a drastically changed situation with an explosion in the Chironomus plumosus population and with the development of a healthy zooplankton including Cyclops Sp. and Daphnia magna. Oscillatoria had become rare while microscopic algae had become numerically abundant. It was concluded that the marked change in the zooplankton and deep water benthos communities was very encouraging but that little change had, or would, occur in the littoral fauna until Polygonum amphibium regeneration took place.

7.1.5. RESULTS OF SURVEYS TAKEN 1981-1984.

Tables 7.3 to 7.8 illustrate quite clearly the significant change in the fortunes of the various species during the decline to 1983 and subsequent explosive recovery. This is illustrated graphically in Figure 7.1 to 7.4 which show the relative numerical abundance of faunal species during early Spring of these years.

During April 1981 (Figure 7.1) it is apparent that pollution sensitive fauna such as caddis fly and mayfly were absent and that Glyptotendipes predominated (with up to 7080 m^{-2}) at shallow water stations, while Chaoborus occured (at up to 1500 m^{-2}) throughout the deeper water. Chironomus was found in smaller numbers. The occurance of Chaoborus appeared to diminish for the other surveys of 1981. However the presence of Chaoborus at the mud surface depends on the turbidity of the water and Figure 7.5 shows a very low chlorophyll-a level, probably associated with fairly clear water at this time. Thus Chaoborus will probably have resided closer to the mud than in more turbid water in October 1981. However all other surveys were carried out at times of relatively low phytoplankton activity, when similar behaviour would be expected.

By February 1982 (Figure 7.2) all of the faunal species had become severely restricted, with Glyptotendipes and Chaoborus suffering most. Reference to Figure 4.4 indicated that this coincided with a time of maximum causticity, with a peak pH 10.5 being reached. Abundance of C.plumosus, low in 1981, seems to have been maintained.

invertebrate: station:	A	B	C	D	E	F	G	H	I	J	K	L	M	N
5														
6	13	3						4						
7	10	4			1			4						
8	5							1						
9	15	8			3									
10	3	105			23				1		(1 Cricotopus)			
11	4	6			2			5						
12	8	4						13						
13	1							31						
14								33						
15								33						
16	3							18						
17		19			1			1	1					
19	2	5			1			11						
20		2	2					21						
21	3							38						
22	1	1						12						
23								4						
24	10	7			1									
25	5	97			1		1		3					
26	4	60			2		1	8	2					
27								1						
28								7						
29	8	2						7						
30	3	4						12						
31	4	2						17						
32	13							1						
33	4	23						6						
34	5	1			1			6			1			
35	11	3						15						
36	7	11												
37	1	1			1			3						
38														
39														
40				8										
41		4		1	7		11							
42	10	133	5		17							7	17	
43	4	66												
44		40			8									
45	4	19						3						
46	14	7			2			2						
47		26			3			2	2					
48	14	177			19									
49		7			2									
50	2	58			3									
51	24	91												

TABLE 7.3. Results of benthic invertebrate survey of April 1981.

A	Chironomus	F	Macropelopia	K	Limnephilus
B	Glyptotendipes	G	Arctopelopia	L	Eiseniella
C	Microtendipes	H	Chaoborus	M	Tubificidae Sp.
D	Brillia	I	Sigara	N	Enchytraeidae
E	Procladius	J	Sialis		

invertebrate: station:	A	B	C	D	E	F	G	H	I	J	K	L	M	N
5	12	5			2			1						
6	5				1									
7	9													
8	6	1												
9	6				4									
10	7	17			3									
11	3	2			1									
12	3													
13					1									
14														
15														
16	10				1									
17		1												
19	5							1						
20	4													
21														
22														
23								1						
24	1	2	1		1									
25	4	21			1									
26	5	30												
27														
28														
29														
30														
31								4						
32	7	3						1						
33	6	2			7									
34	14				2									
35	7				1									
36	7													
37	2													
38					1									
39														
40														
41					1									
42														
43	1				3									
44	1	1			1									
45	3				1									
46	4	1			2			2						
47	4	2			2									
48		12												
49		6			11									
50	3	6			1									
51	2	36			7								3	

TABLE 7.4. Results of benthic invertebrate survey of July 1981.

A	Chironomus	F	Macropelopia	K	Limnephilus
B	Glyptotendipes	G	Arctopelopia	L	Eiseniella
C	Microtendipes	H	Chaoborus	M	Tubificidae Sp.
D	Brillia	I	Sigara	N	Enchytraeidae
E	Procladius	J	Sialis		

invertebrate: station:	A	B	C	D	E	F	G	H	I	J	K	L	M	N
5	3				3									
6	5							1						
7	9	1			1									
8								2						
9	2				1									
10					1					2				
11					3				1	1				
12	5				1									
13	1							8						
14								20						
15								7						
16	6								1					
17														
19	13	1			2									
20								2						
21	1	1						2						
22								2						
23								1						
24	10	2												
25		186							2					
26		22							5					
27														
28														
29	1							3						
30	9							3						
31	3	1						1						
32	13	1												
33	13				2				(1 Cricotopus)					
34	21													
35	9	1												
36	18													
37	10	4												
38														
39														
42														
43														
44	4	1			1									
45	15	3			2									
46	7				6									
47	13	1		5	1									
48		23			13							1		
49		15		1										
50														

TABLE 7.5. Results of benthic invertebrate survey of October 1981.

A	Chironomus	F	Macropelopia	K	Limnephilus
B	Glyptotendipes	G	Arctopelopia	L	Eiseniella
C	Microtendipes	H	Chaoborus	M	Tubificidae Sp.
D	Brillia	I	Sigara	N	Enchytraeidae
E	Procladius	J	Sialis		

invertebrate: station:	A	B	C	D	E	F	G	H	I	J	K	L	M	N
5			1						1					
6	6													
7	4								1					
8	6				2									
9	7				2			1						
10					4									
11	1				1									
12	1				1									
13								1						
14								3						
15								4						
16	5													
17														
19	8				1									
20								7						
21								1						
22								4						
23														
24	7				2									
25													95	
26		42							2					
27														
28														
29		1						1						
30	2													
31								6						
32	10	1			3									
33	9				3									
34	15													
35	8				1			1						
36	11									(1 Lymnaeidae)				
37	5													
38														
39														
40														
41					5							2	5	
42										1		1	28	
43	4	4			5									
44	15				1									
45	4	3		1	2									
46	8				3									
47	5	1			1									
48		28			9									
49														
50	1	5			8									
51														3

TABLE 7.6. Results of benthic invertebrate survey of February 1982.

A	Chironomus	F	Macropelopia	K	Limnephilus
B	Glyptotendipes	G	Arctopelopia	L	Eiseniella
C	Microtendipes	H	Chaoborus	M	Tubificidae Sp.
D	Brillia	I	Sigara	N	Enchytraeidae
E	Procladius	J	Sialis		

invertebrate: station:	A	B	C	D	E	F	G	H	I	J	K	L	M	N
5														
6	1													
7	2													
8														
9	3													
10														
11	11	1			3									
12														
13														
14														
15														
16														
17	2													
19														
20		1	5		8									
21														
22			1					1						
23														
24														
25	2				1				2	1				
26	26	8	46											
27	11		40		1									
28														
29	7													
30	21		1	1	1									
31	1													
32														
33	8		1											
34	13	1												
35	4	1												
36	1													
37	5				1									
38	8													
39														
40														
41												9	2	
42			8	1								4		2
43	23	18	18	24	4						6			
44	9	4	32	1	4						6			
45	1			1										
46														
47	2		1						2					
48	12		1											
49	2				2									
50	3	3	1		1									
51	1		2		1	1								

TABLE 7.7. Results of benthic invertebrate survey of March 1983.

A	Chironomus	F	Macropelopia	K	Limnephilus
B	Glyptotendipes	G	Arctopelopia	L	Eiseniella
C	Microtendipes	H	Chaoborus	M	Tubificidae Sp.
D	Brillia	I	Sigara	N	Enchytraeidae
E	Procladius	J	Sialis		

invertebrate:	A	B	C	D	E	F	G	H	I	J	K	L	M	N
station:														
1	1													
2	21	1	5		20									
5	35				1									
6	28	2												
7	52													
8														
9	31	1			2									
10	25													
11	52				2									
12	59													
13	39													
14	7													
15	17													
16	50				1									
17														
19	27													
20	52													
21	44							3						
22	4													
23	43								2					
24	38						1							
25	150		4						2					
26	71	2	9		5					1				
27	34													
28	30						1							
29	18													
30	46	1												
31	58													
32	24													
33	29	2			3									
34	50	1												
35	68													
36	32													
37	34				2									
38	37				5									
39														
40			11		1		(1 Eukiefferiella)				2			1
41			14	4			3		1		1	3	4	1
42			1											
43	10		1		5									
44	72	4	11		16									
45	13	1	2		5				1					
46	39				2									
47														
48	24	1	4		15									
49														
50	73	14	3		16									
51			1											

TABLE 7.8. Results of benthic invertebrate survey of April 1984.

A	Chironomus	F	Macropelopia	K	Limnephilus
B	Glyptotendipes	G	Arctopelopia	L	Eiseniella
C	Microtendipes	H	Chaoborus	M	Tubificidae Sp.
D	Brillia	I	Sigara	N	Enchytraeidae
E	Procladius	J	Sialis		

FIGURE 7.1.

Distribution of benthic invertebrate larvae - Spring 1981.

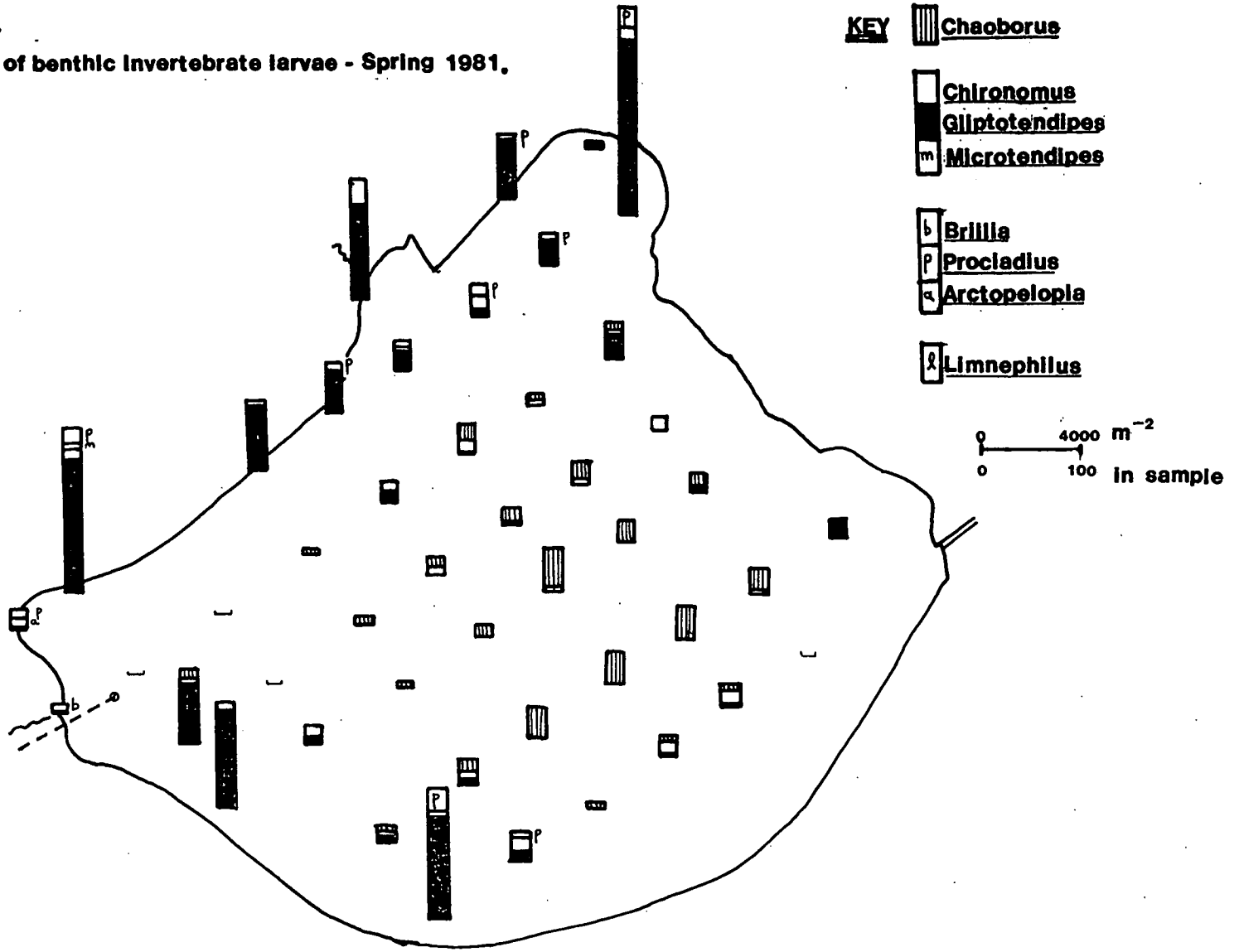


FIGURE 7.2.

Distribution of benthic invertebrate larvae - Spring 1982

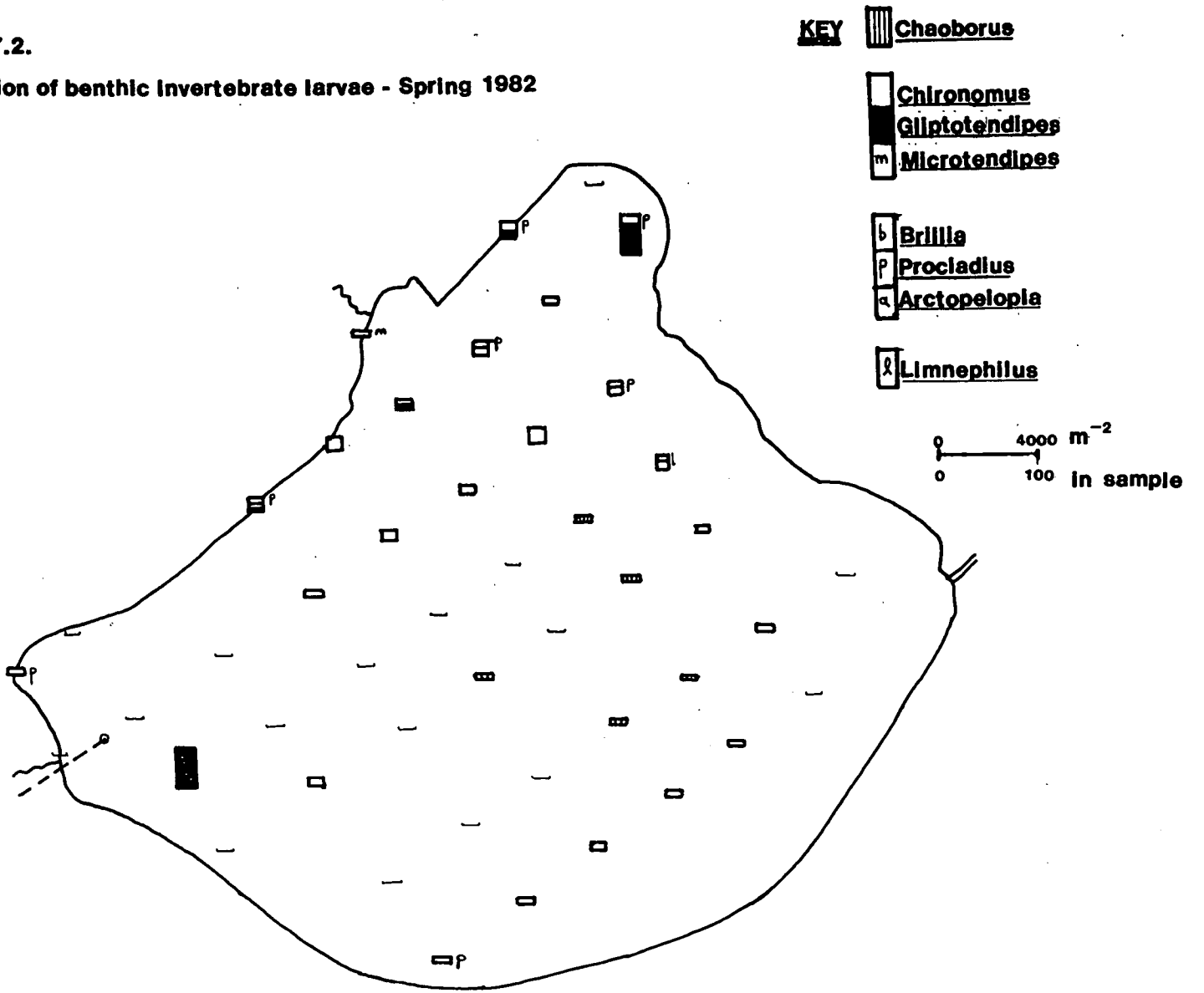


FIGURE 7.3.

Distribution of benthic invertebrate larvae - Spring 1983

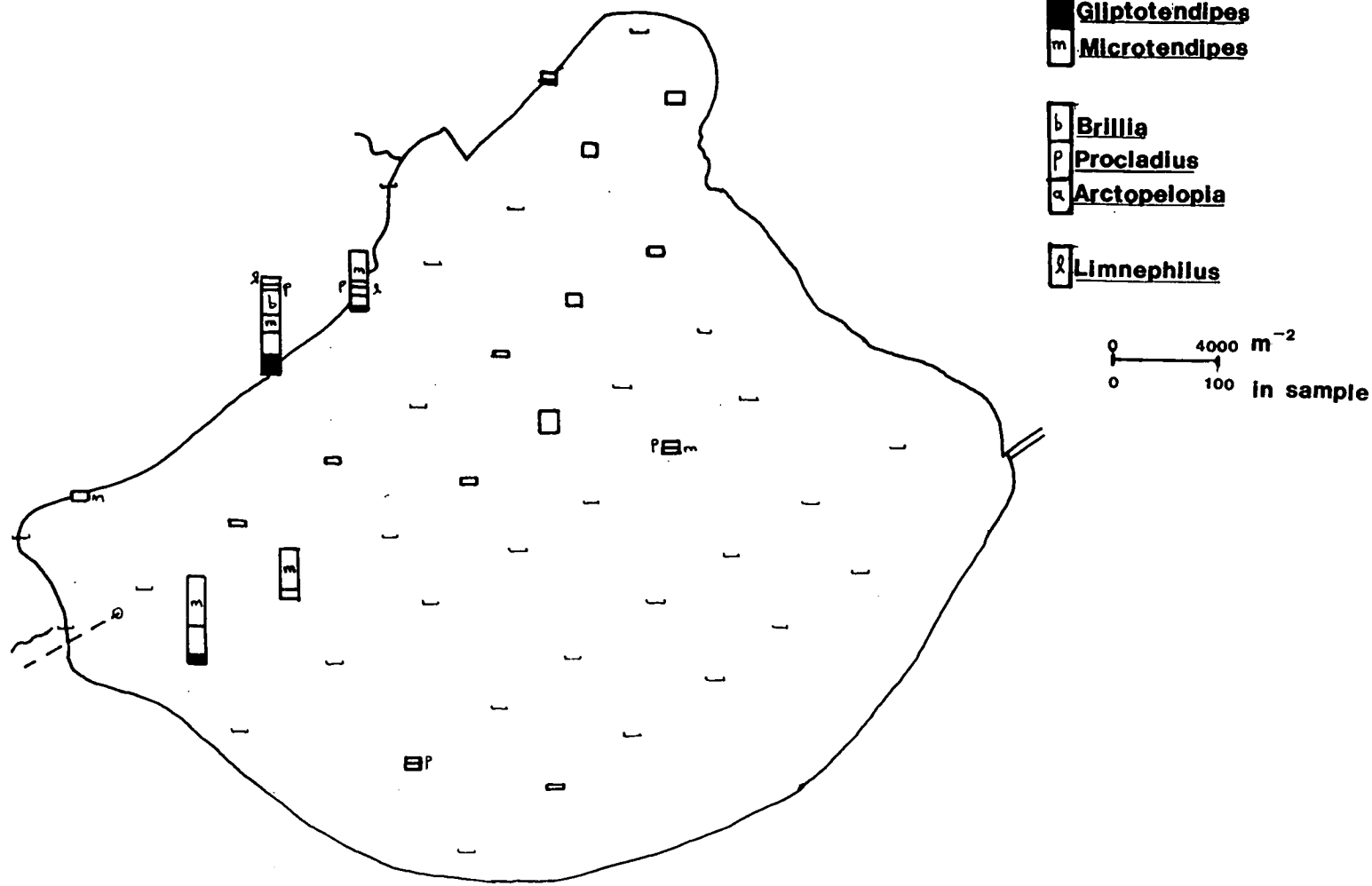
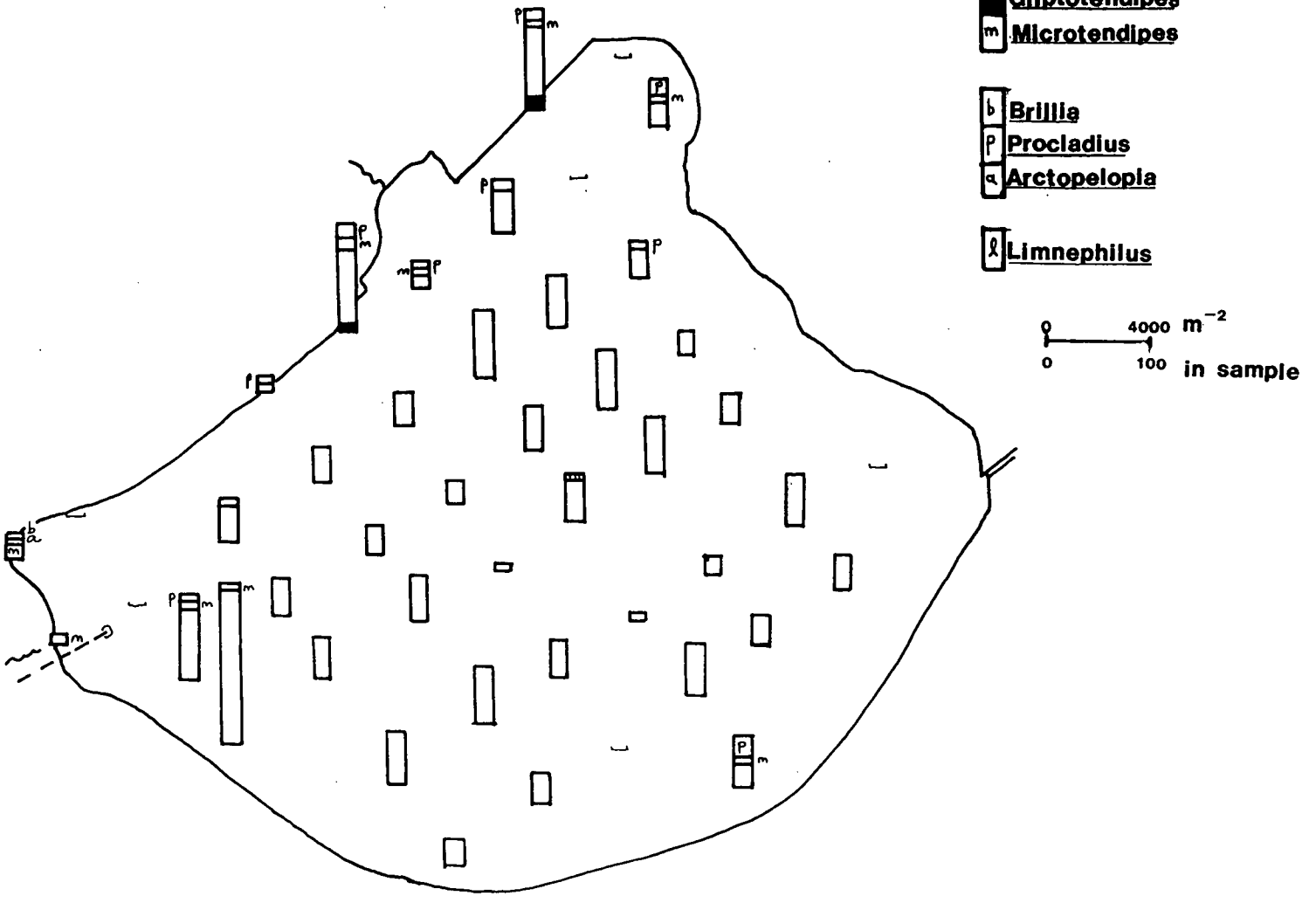


FIGURE 7.4.

Distribution of benthic invertebrate larvae - Spring 1984



March 1983 shows a similar situation (Figure 7.3) but with Chaoborus and Glyptotendipes further restricted. For some reason which is not understood, Microtendipes, a pollution-intolerant genus appeared to have begun to colonise certain stations, even though the mean pH remained above 10. Stations 26 and 27 were on the route of the softest mud travelling from the leachate to the deeper parts of the loch (Figure 5.3) but it was these stations which became colonised.

With the removal of the leachate in May 1983 the loch began to recover rapidly and by April 1984 the pH had dropped to 8.4 and chlorophyll-a reduced to <10 ug l^{-1}. Figure 7.4. shows an explosion of C.plumosus of up to 6000 m^{-2} with a mean over the whole of the loch of approximately 1000 m^{-1}. The occurence of Microtendipes had decreased to very low levels and Glyptotendipes had not recovered. Despite the abundant zooplankton that had developed, providing a plentiful prey for Chaoborus, Chaoborus showed no sign of recovery with only 3 animals being found.

It is probable that Microtendipes cannot colonise the loch due to the continued presence of toxic metals in the interstitial water of the sediment (see Chapter 5.5) and the Chironomus will remain dominant for some time. It would be expected that Chaoborus would return to prey on the zooplankton.

7.2. PLANKTON.

Plankton samples taken from Kinghorn Loch prior to 1984 have consisted almost entirely of Oscillatoria. Zooplankton had remained very sparse. Figure 7.5 charts the levels of chlorophyll-a found from 1981 to the end of 1984 and shows the development of very

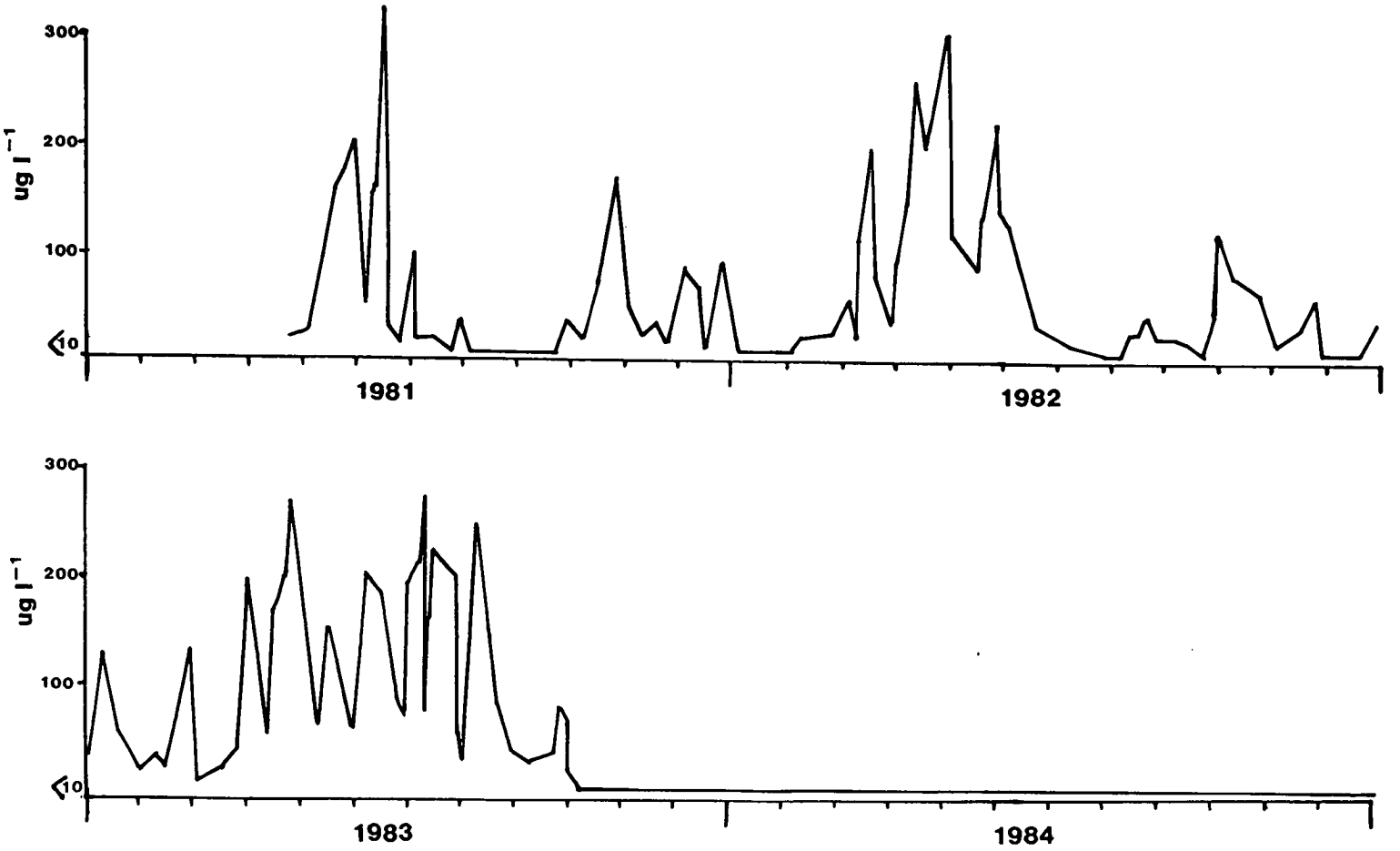


FIGURE 7.5. Levels of chlorophyll-a found at the outlet for 1981 to 1984.

substantial blooms. Significant blooms did not occur above pH 10 and it is possible that carbon may become a limiting nutrient at such high pH. According to Reynolds[39] carbon dioxide would not exist at a usable level and phytoplankton growth would be limited, unless HCO_3^- can be used. Even so high productivity could not be maintained. Reynolds reported that photosynthetic rates may be maximal at pH 9-10, although restricted at pH >10 due to the toxic effects of pH *per se*. He considers the reason for this maximal activity to be unclear.

Oscillatoria may well have an advantage in a stressful situation like this by being mobile and able to adjust position, both lateral and vertical, to make best use of any bicarbonate available. This mobility also allows adjustment for the receipt of optimal illumination in a permanently cloudy body of water.

The role of phytoplankton on the chemistry of the loch has been extensively discussed in Chapters 4.7 to 4.9. The most significant feature in Figure 7.5 is the collapse of phytoplanktonic activity since October 1983. Although phosphorus input to the loch became extremely low, the existence of such an abundant zooplankton, and in particular of *Daphnia magna*, a species found in alkaline, nutrient-rich environments, must indicate an appreciable nutrient supply from the sediment. This supply would be taken by algae which are then grazed extensively by the zooplankton. It is generally considered that *Oscillatoria* is not grazed by zooplankton, and the introduction of zooplankton cannot explain its collapse. It is possible that competition for nutrients with algae and the generally lower level of supply may have been contributing factors.

CHAPTER EIGHT

CONCLUSION

8.1. AQUEOUS INPUTS TO THE LOCH.

Water is retained in Kinghorn Loch for an average 245 days. During the period of study the water body was found to be generally well mixed with only occasional stratification during particularly prolonged periods of calm, warm weather. The mean flow of the north inlet (past Craigencalt Farm) was 15.3 l s^{-1} of which it was calculated that 25% originated as groundwater from basaltic tuff aquifers. This inlet contained a substantial level of nitrate (7.3 mg l^{-1}) and of dissolved silica (4.3 mg l^{-1} as Si) and was quite "hard", with a calcium level of 43 mg l^{-1} and with magnesium at 22 mg l^{-1}. It possessed a naturally high pH value of around 8.1. Because of the irregular discharge of water from the loch via the penstock it was difficult to calculate the ingress of non-discrete native water to the loch but it was calculated that 32±14 % of incoming water was from such sources. It was considered that, as all non-discrete percolate will have originated on basalt or basaltic tuffs, its chemistry would be similar to the north inlet water. However several local springs rising on the lower edge of the basalt were known to be of high sulphate and sodium content and any significant proportion of this composition of water would cause significant errors in the calculation of losses of material to the sediment. Many of these springs may represent water polluted by red mud leachate or from the mining activities of the nineteenth century.

The interstitial water of the red mud, from which the leachate was derived, was known to be clear, colourless and low in organic material. During its progress from the tip the leachate dissolved substantial quantities of soil organic matter to impart a deep brown colour and, at the same time, substantial quantities of aluminium

were lost from the leachate. This loss represented some 1000 mg l^{-1} with the final concentration in the emergent leachate being between 11 and 240 mg l^{-1}. It is proposed that such a loss occured by solubilisation of soil-derived silicon (silt or sand) with subsequent subterranean deposition of sodalite or zeolite-type minerals.

It was estimated that the leachate became diluted with five times its volume of native water prior to reaching the loch. The leachate was the prime contributor to the loch of causticity, arsenic, vanadium, aluminium, phosphorus (as orthophosphate), sodium, and sulphur (as sulphate) while the native water provided calcium, magnesium and silicon. Neither input contributed substantial quantities of organic matter. Red mud solids, washed in with the leachate, provided virtually all of the iron contained in the loch. The ratio of leachate to combined native water inputs was approximately 1:7.7.

By 1983 the pH of the loch had risen to a mean of 10.1 and suffered intense phytoplanktonic blooms, consisting almost entirely of Oscillatoria, with little zooplankton or diatoms present. The invertebrate population had decreased rapidly and while Chaoborus had been abundant in 1981, it had become virtually absent. The abundance of the dominant invertebrate, larvae of Chironomus plumosus, had decreased greatly and littoral flora had largely disappeared.

Although ingress of the leachate had begun in 1954, significant quantities did not enter until 1961 when the pH began to increase. This rise accelerated after 1978 so that by 1983 the mean pH exceeded 10.1. By this time Kinghorn Loch carried by far the highest concentration of dissolved arsenic (and undoubtedly vanadium) of any

watercourse in the United Kingdom, being sampled at 500 ug l^{-1} (compared with a normal unpolluted level of 5 ug l^{-1}).

The inlet waters, leachates and loch water were sampled on a weekly basis from 1981 to 1983 in order to obtain an estimate of the losses of material to the sediment. This sampling frequency gave an estimate of long-term concentration to within 10%, but only to 20% for flow related loadings. Calculated losses to the sediment proved to be well in agreement with the elemental levels found in the sediments, and allowed the identification of additional atmospheric inputs and of losses from the sediment-water body system. All determinands contained within the loch water were surprisingly poorly correlated, and (for instance) chlorophyll-a could not be related to nutrient status. Although the water was generally well mixed, local reduction zones occured and these were characterised by low dissolved oxygen and very high electrical conductivity, dissolved calcium, magnesium, aluminium, arsenic and iron. Alkalinity was elevated and free sulphide occured.

A thermodynamic equilibrium mathematical model was developed in order to calculate the aqueous speciation of determinands within the loch, and to determine which minerals could potentially be formed. The model was based on WATSPEC. The WATSPEC core was linked to procedures to allow the input of mixing waters and included instantaneous adjustment of pH and alkalinity. Following speciation, procedures were employed for the deposition of minerals that the model indicated could be formed. Despite various modifications, intended to model kinetic considerations, it was concluded that insufficient data was available concerning kinetic mechanisms to

allow any meaningful considerations to be given. The exercise indicated the severe limitations that exist in attempting to apply a thermodynamic model to the real system, and the apparent total lack of usable kinetic data. WATSPEC is said to require input data at a precision of better than 5% for accurate speciation, and it is evident that the long-term mean data for the loch, even with such an intense sampling programme, did not meet this criterion.

The model was used to determine starter concentrations and pH for various laboratory experiments, in order to avoid possible precipitation of particular minerals during the experiment, and in this context it was successful.

The processes which controlled aqueous chemistry within the loch were the formation and sedimentation of calcite and the prolific phytoplanktonic activity. Both processes led to the mineralization of various lesser components of the aqueous system. By 1983 it was observed that sedimentation was impeded by the surface charge repulsion at such high pH values, and phytoplanktonic debris was substantially degraded prior to reaching the mud-water interface.

It was considered that at least 60% of the carbon derived from phytoplanktonic activity was recirculated by degradation prior to reaching the sediment. It appeared that virtually all of this carbon was obtained directly from the atmosphere and not from carbonate derived from the leachate. Most of the carbonate used for calcite formation was leachate derived although Figure 4.8 indicates that at least some of the calcite was of biogenic origin or that the carbonate ions had been biotically generated. Uptake of atmospheric

carbon dioxide to the water body was of minor importance with regard to the inorganic chemistry and the lack of equilibrium with the atmosphere was evident, and predicted by the model.

8.2. LOSSES TO THE SEDIMENT.

Laboratory experiments indicated that calcite production occured without the inclusion of humic materials and proceeded by second order kinetics. This order would suggest that interference occured to prevent crystal growth by spiral dislocation and that growth was related to surface area. Magnesium, phosphate and sulphate inclusion are known to interfere in this way (Reddy[63,64]). Silicon, magnesium and aluminium were lost to the sediment in the proportion of 1:2.8:5, indicating the probable formation of mixed layer clay minerals, possibly of chlorite-montmorillonite type containing brucite layers (Weaver & Pollard[105]). Laboratory experiments suggested that the rate of formation and sedimentation of clay minerals was independant of calcite production and that co-precipitation processes were not dominant.

Phosphorus and nitrogen were probably lost to the sediment by way of phytoplanktonic debris, although phosphorus may also have been chemisorbed onto hydrous iron oxides or included as surface complexes on calcite. Arsenic and vanadium are readily soluble at high pH but nevertheless were removed to the sediments. Arsenic becomes concentrated in plankton and may well have been taken to the sediment in debris. The ultimate sink in the sediment would be on hydrous iron oxides and this may have occured within the water body. Vanadium was most likely to have been lost by sorption onto humic solids.

It was estimated that 80000 kg of authigenic calcite and 40000 kg of authigenic clay minerals reached the sediment each year along with 26000 kg of organic material derived from phytoplankton. In comparison detrital inputs were estimated to total 20000 kg, comprising wweathered rock products, iron and clay minerals from red mud and some humic matter. The mean total deposition rate for 1981-1983 was calculated to be 1.5 kg m^{-2} yr^{-1}.

8.3. SURFICIAL SEDIMENTS.

Surficial sediments within the deeper parts of the loch were found to consist of very fine thixotropic muds of high moisture content. The most liquid muds were found around the leachate entry and a 'slick' of wet mud progressed from this area toward the deepest part of the loch. Moisture contents were high in 1981, but became progressively higher until the removal of the leachate in 1983. The effect of this progression and its ultimate reversion during the recovery of the loch was evident in the volume of the upper parts of the sediment cores and was related to prevailing pH and ionic strength.

Larger particle sized material was richer in silicon (presumably detrital quartz) while the finest particles appeared deficient in calcite and possibly richer in organic material. Clay minerals were distributed throughout the sizes.

8.4. SEDIMENT CORE PROFILES.

Organic matter throughout the core profiles was found to be degraded to a considerable degree, although apparently fresher in shallower water away from the leachate entry. The C:N ratio indicated a high degree of humification, probably occuring mainly within the water

body.

Because of the thixotropic nature of the sediment it was not possible to obtain interstitial water by normal techniques. Eventually it was decided to obtain water from thawed samples after deep freezing, while maintaining oxygen-free conditions. Investigations into the effect of the treatment failed to find significant error, although the alteration of surface characteristics and physical environment so caused, was undoubtedly profound.

Redox potential was measured in the cores, and the potential was found to become negative within approximately 20 mm of the sediment surface. The electrometric potential so measured is sensitive to iron and arsenic transformations but not to the C-H-N-S-O processes (Drever[77]). However this appeared adequate to indicate extremely reducing conditions in the cores. At such high pH values many transformations occur below the -250 mV minimum instrument reading (see Figure 5.26). The interstitial water chemistry indicated that reduction processes were occuring. It would appear from the results that methane fermentation was a primary process, resulting in the solubilization of calcite, which would act as an acidity regulator, the process being otherwise subject to acidity limitation. Although nitrate and iron were involved in reduction reactions, sulphate was never fully reduced and this was due to the lower Eh required at elevated pH. Reduction processes were characterised in the interstitial water by high levels of iron, calcium, aluminium and arsenic with low nitrate and the occurance of free sulphide.

Cluster analysis provided relativity within and between the cores.

The grey zones in cores 14 and 39 appeared to be composed of fine sediment and not visually related to the dark fibrous "native" material below. However these zones proved to be poorly correlated with the similarly textured material above, but well correlated with the fibrous material.

It is considered that the grey zones represented a time (approximately 1954-1965) when phytoplanktonic activity had increased due to the phosphorus input of the infant leachate. Such activity will have limited macrophyte growth but substantial calcite and clay mineral formation was not yet occuring. During this time a substantial supply of manganese and sulphur was available from the fibrous "native" material, with additional sulphur coming from leachate-derived sulphate. Pyrite is often considered to form under such conditions (Berner[118],Howarth[127]) and this grey colour indicates the occurance of substantial quantities of pyrite. Despite the high sulphate input of the leachate substantial quantities of sulphur have not become available in more recent times because of the rising pH, and therefore once this transition zone became buried, further substantial pyrite formation would not be expected to occur. It appears from the horizons found within the manganese and acid volatile sulphur profiles that this original sink of manganese and sulphur continued to provide the upper parts of the cores with a limited supply of these elements.

The proportion of calcite in the red/red-brown parts of the cores increased steadily from 1962 onwards with an increasing flow of leachate entering the loch. Strontium correlation with calcium indicates that essentially all of the calcium was present as calcite.

It would appear that the type of clay minerals present changed considerably from the early 1960's to 1983. Initially silicon was the dominant clay forming element. As the pH increased this dominance gradually disappeared and, with the pH ultimately exceeding 10.1, magnesium became dominant. It is probable that a montmorillonite mineral will have formed with a high silicon content but, as the water became supersaturated with respect of brucite, mixed layer chlorite-montmorillonite may have formed with brucite layers.

The correlation of rubidium and potassium with silicon indicates a gradual change in clay mineral character with a supply of suitable lattice positions decreasing in approximately the same proportion as the silicon content. The correlation of zinc with silicon indicates the presence of a moderately constant proportion of a zeolite or similar mineral within the clay content. Aluminium and silicon were found to be inversely correlated in the interstitial water and this provided evidence for an active equilibrium operating between the aqueous phase and the authigenic clay mineral phase.

Vanadium and arsenic show surficial enrichment in the sediment and are evidently mobilised by reduction-oxidation processes affecting iron oxides. Arsenic is deficient in the sediments and is probably released continuously from the sediments as arsines.

Sedimentation rate was calculated by ^{137}Cs and ^{210}Pb radionuclide dating. Because of the turbation of the sediments and lack of suitable substrate ^{137}Cs dating was unsuccessful. ^{210}Pb dating predicted a deposition rate for the "native" sediment of 1.5 mm yr^{-1},

and the data supports a mean sedimentation rate for 1962-1983 of 15.7 mm yr^{-1}. It was calculated that this rate varied from near 2-5 mm yr^{-1} in 1962 to 25 mm yr^{-1} in 1983. Several problems existed in the application of ^{210}Pb dating to this system but it is considered that data manipulation procedures used (Chapter 5.6) compensated reasonably well for these.

8.5. RECOVERY.

After the removal of the leachate in May 1983, the quality of the loch water improved rapidly. This was due, at least in part, to the drawdown of the water surface during sluice renovation work, followed by a rapid refilling with the winter run-off. However, despite a lowering of the pH to that of the north inlet, the survey of April 1985 showed that a considerable amount of arsenic was potentially available to the interstitial waters within the upper parts of the cores, and thereby to the body of the loch. In consequence the water body only narrowly complied with the Environmental Quality Standard (EQS) of 50 ug l^{-1} applied to freshwater fisheries. It is likely that this release will continue for several years. The core taken in 1985 showed continuing redox reactions within the interstitial water although the Eh had improved throughout its length. Analysis showed that the plankton population that had grown up in place of the rampant Oscillatoria blooms did not concentrate arsenic and neither did the invertebrate population. Thus the plans of Kirkcaldy District Council to stock the loch with rainbow trout can be safely supported, although further arsenic (and vanadium) surveys should be undertaken during calm, warm weather. The number of invertebrate larvae in the sediment had increased greatly and, although presently not diversified, must be a good indication for the rehabilitation of

the loch. The lack of any problems with regard to phytoplankton activity indicates that the loch water had reverted to an oligotrophic state. Surprisingly, Chaoborus, which would have been expected to rapidly recolonise the loch with the advent of abundant zooplankton prey, has not done so. It is probable that the drastic decline in numbers from 1982 to 1983 left an insufficient number of individuals to affect such a recovery.

8.6. FUTURE INVESTIGATIONS.

Considerable effort is still required in order to elucidate the clay mineralogy of the loch. The sediment is relatively free of detrital input and provides a unique opportunity for testing a theory of authigenic clay mineral production over a very short geological time scale. This is in contrast to the efforts of other workers currently researching this subject (e.g. Mackin & Aller[100]), operating in relatively dirty situations where the authigenic component is minor relative to detrital input.

A similar situation exists concerning the theory of pyrite formation (Berner[118], Howarth[127]) and the advantages of such a study in Kinghorn Loch are again evident.

The natural aquatic chemistry of vanadium has been neglected, and interest in its toxicity is very recent, with the situation currently being reviewed by the Water Research Centre under contract to the Department of the Environment. The sediments of Kinghorn Loch continue to provide a natural situation of high aquatic vanadium content, for the study of vanadium speciation, as does the Kirkton Burn, currently exposed to leachate ingress.

An ongoing monitoring programme is needed to ensure that no toxic effects are encountered in the stocking of Kinghorn Loch with rainbow trout. Arsenic and vanadium are likely to continue to be released from the sediments for some years.

CHAPTER NINE

ANALYTICAL PROCEDURES

9.1. CHEMICAL ANALYSIS OF AQUEOUS SAMPLES.

All chemicals used were of analytical quality grade unless stated otherwise. All water was once-distilled using a glass bodied still fitted with an all-glass receiving and collection system. Distilled water used for the analysis of metal ions was deionised prior to use.

9.1.1. SAMPLING AND PRE-ANALYSIS PREPARATION.

9.1.1.1. SAMPLING PROCEDURE FOR "ROUTINE" DETERMINANDS.

Samples were collected on a weekly basis from January 1981 to provide analytical data on the leachate entering Kinghorn Loch, the north inlet and the loch outlet, and irregularly for water body stations. Samples were taken in 1000 cm^3 glass bottles (250 cm^3 for water body stations) provided with polypropylene screw caps. The bottles were cleaned in 50% v/v chromic acid solution and thoroughly rinsed and drained prior to use. Samples were taken at mid-depth in running water or at 0.3 m for loch water at the outlet. All bottles were twice rinsed with sample prior to collection proper. All bottles were filled to within 5 mm of the cap. Water body sampling at various depths was achieved using a Cassela-type sampler suspended on a line marked in m. The sampler consisted of a weighted cylinder containing the sample bottle and capped with a cap containing two tubes. The central tube entered the bottle with the outer tube raised above the level of the cap. The tubes were sealed with silicone rubber bungs which, at the required depth were remotely removed allowing water to pass through the bottle until the sampler was filled.

Where sub-samples were required for the determination of dissolved oxygen or dissolved sulphide, 125 cm^3 glass bottles fitted with polypropylene stoppers were used. The sample bottle was filled

without entraining air and stoppered. Preservation of the determinand was carried out immediately. For dissolved oxygen this involved adding 1 cm^3 50% w/v manganese(II) sulphate solution followed by 1 cm^3 alkaline iodide solution(150 g KI + 700 g KOH l^{-1}) and stoppering so as to exclude all air[155]. Sulphide was preserved by adding 1 cm^3 0.5 M zinc acetate solution followed by 1 cm^3 0.75 M sodium carbonate solution[156] and stoppering so as to exclude all air. The sub-samples were inverted several times and, on return to the laboratory, analysed immediately or stored in a cool, dark place and analysed within 24 hours.

Sub-samples for chlorophyll-a determination[157] where filtered on station by the use of a hand pump. 30 cm^3 was used if a phytoplankton bloom was evident and 200 cm^3 if absent. A blank filtration using distilled water was always carried out and this was followed by duplicate filtrations of the sample. Each was filtered through a 0.45um membrane, with 0.2 cm^3 of a suspension of 10 g l^{-1} magnesium carbonate being added to the last few cm^3 in the filter funnel. After filtration the membrane was inserted into a 30 cm^3 screw cap (PTFE coated silicone rubber insert) test tube and 5 cm^3 90% v/v acetone in water added. The tube was thoroughly shaken and agitated to get the membrane to the bottom of the tube. The tubes were wrapped in a piece of aluminium foil and after return to the laboratory kept at 4°C for 24 hours prior to analysis.

Instantaneous flow was recorded by reference to gauge boards (at north inlet and below loch outlet) or by depth of water flowing over a 'V' notch weir for the leachate [and later the west inlet (same discharge point)]. Flow at the north inlet during low flow

conditions was measured by timing the collection of 20 l of water exiting the mill lade.

Samples were returned to the laboratory within two hours of collection (except for evening samples which were stored in a cool, dark place overnight). Preparation for analysis was immediately undertaken according to the procedure outlined in Figure 9.1 for leachate, inlets and loch at outlet, or Figure 9.2 for water body stations.

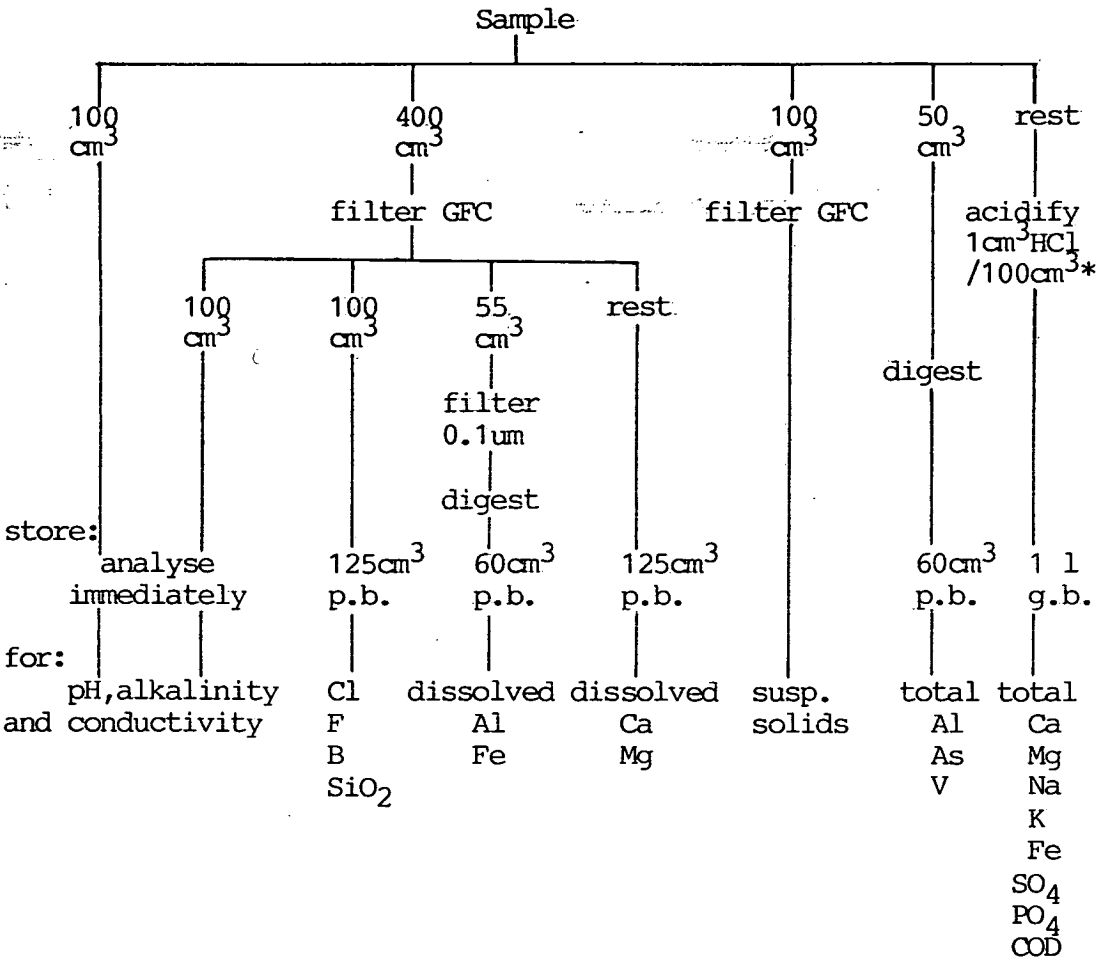


FIGURE 9.1. Pre-analysis division of samples for leachate, inlets and loch at outlet. Notes: p.b.=polythene/polypropylene bottle, prewashed as necessary, g.b.=glass bottle - use existing sample bottle, *=acidify leachate at $2cm^3/100cm^3$, digest=see appropriate analytical method

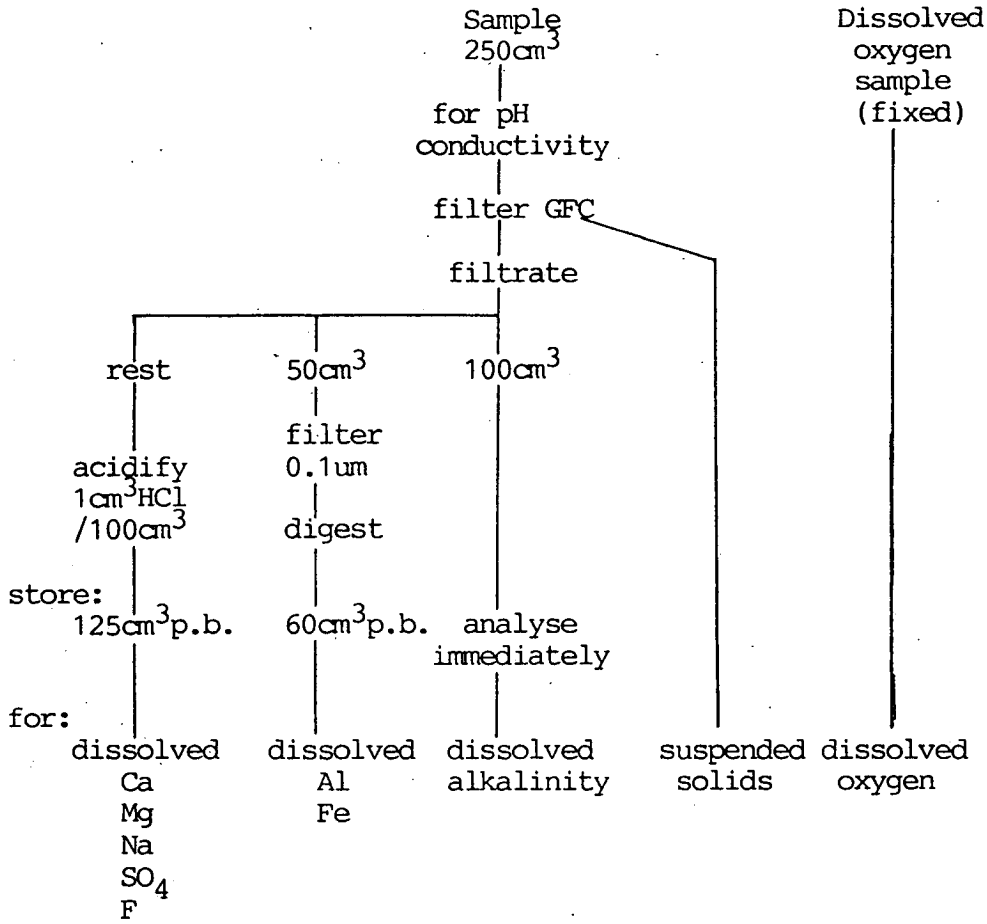


FIGURE 9.2. Pre-analysis division of samples for water body stations. Note: p.b.=polythene/polypropylene bottle prewashed as necessary.

Many workers consider that material passing a 0.45um membrane may be considered to be dissolved. This assertion is in part due to a necessary compromise because of the difficulty often experienced in passing raw water through a finer membrane. However Kennedy et al[158] found that fine-clay sized particles can pass a 0.45μm membrane and cause major errors in the determination of "dissolved" aluminium, iron, manganese and titanium at trace levels. Wagemann & Brunskill[159] investigating the effect on "dissolved" iron, aluminium, silicon and magnesium found that, while silicon and magnesium were unaffected by pore size, iron and aluminium (at 0.5 mg l^{-1} and 0.1 mg l^{-1} respectively) were reduced by approximately half when filtered at

0.1μm rather than 0.45μm. Thus it was decided that for these two metals filtration should be carried out using 0.1μm membranes. In practice it was found that difficulty with filtration occured only with water from the loch and only then at times of planktonic activity.

9.1.1.2. SAMPLING PROCEDURE FOR TRACE METAL ANALYSIS.

On occasions during the study analysis was carried out for trace metals other than routinely determined total arsenic and vanadium. Samples of leachate were collected in 1 l polythene or polypropylene bottles fitted with unpigmented polypropylene screw caps while inlet and loch water samples were collected in 10 l polythene bottles. All bottles were previously steeped in 50% v/v nitric acid solution for 24 hours, thoroughly rinsed with deionised water and drained. Immediately upon return to the laboratory samples intended for dissolved metal analysis were filtered through previously acid and water washed glass fibre discs and then through 0.1μm polycarbonate filter membranes. Samples of leachate were adjusted to pH2-4 with 1 M spectrophotometric grade hydrochloric acid. 2 cm^3 l^{-1} spectrophotometric grade concentrated hydrochloric acid was added to all samples as preservative[160] to await analysis. All samples were evaporated on a hotplate to approximately 80 cm^3 in acid washed beakers covered with watch glasses. Acidified deionised water was similarly treated. Care was taken to avoid further volume reduction due to the risk of etching alumina anti-bumping granules. Samples were made to 100 cm^3 with deionised water and stored in acid-washed 125 cm^3 polypropylene bottles with unpigmented caps. This procedure achieved a concentration of north inlet and loch water of 100 times and of leachate of 10 times. Prior to mid-1984 samples were analysed

by flame atomisation Atomic Absorption Spectrophotometry except for cadmium and lead which were determined by graphite furnace atomisation. After this time Cd, Pb, Ni, Cu, Cr and Mn were all determined by furnace except for total Mn and Zn.

9.1.2. ANALYTICAL PROCEDURES FOR AQUEOUS SAMPLES

Techniques reviewed in this section are those generally applied by water pollution laboratories and are described in a number of authoritative text books. Thus, only the general principle of analytical technique, together with modifications applied during the study, will be given. Relevant comment such as possible interference will also be covered. The main reference is given immediately following the determinand name.

9.1.2.1. OXYGEN DEMAND.

Dissolved Oxygen[155]. All routine measurements were carried out by "fixing" a sub-sample on station as manganese(III) oxyhydroxide by adding manganese(II) sulphate and alkaline iodide. On the addition of sulphuric acid iodine is released which is titrated against sodium thiosulphate solution. The percentage saturation of oxygen in the water may then be calculated by reference to tables at the particular sampling temperature. No correction was made for ionic strength of the loch water - error from this source being insignificant. Interference by nitrite was avoided by the addition of sodium azide to the alkaline iodide. Some of the water body surveys were executed using a dissolved oxygen sensitive probe giving automatic temperature compensation and direct readout. It is the experience of the author that the use of such in the field can generate bias in excess of ±10% (at 95% c.l.) and field readings were always checked against "fixed"

sub-samples determined by titrimetry.

Biochemical Oxygen Demand[161]. $B.O.D._5$ is a determination of the oxygen depletion within a sample held in darkness at 20°C for 5 days due to carbon assimilation by microorganisms. Samples of water from the loch required an initial adjustment of pH with orthophosphoric acid to pH 6.5-7 and a microorganism seed to be added by way of a spike from the effluent of a good quality sewage treatment works. Capsules containing suitable cultures for seeding are also now available. Excessive variation in pH was avoided to allow the loch water to retain its own suite of microorganisms as far as possible, since these would be acclimatised to the potentially toxic metals in the water. BOD_5 was determined with the addition of allyl thiourea to suppress demand from the oxidation of ammonia. Because Nitrosomonas may or may not be present and because it is slow to culture, this suppression improves the precision of the method. Due to the potentially toxic materials in the loch the reliability of the method must be brought into question. The BOD_5 is predominantly derived from the breakdown of phytoplankton in the sample during the test.

Chemical Oxygen Demand[162] and Permanganate Value[163]. These determinations have been referred to in the text and references should be consulted for procedure.

9.1.2.2. POTENTIOMETRIC DETERMINATIONS.

pH Value[164]. pH was determined using a Radiometer PHM 63 meter with direct digital readout. The combination electrode was calibrated against pH4 (phthalate), pH7 (orthophosphate) and pH9 (borate)

buffers, the exact pH of the buffer at ambient temperature being noted from tables in the stated reference or supplied with the buffer.

Electrical Conductivity[164]. This was determined using a Radiometer CDM 3 conductivity meter. The meter was calibrated against 0.1 M potassium chloride solution, the conductance of which was obtained from tables for the ambient temperature. Precision is considered to be much better than 5%.

Fluoride[165]. Fluoride was determined using an ion selective electrode with a separate standard calomel reference electrode. The method is sensitive to interferences, particularly hydroxide calcium, iron and aluminium but the use of a suitable buffer containing CDTA (trans-1,2,diamino-cyclohexane-N,N,N',N'-tetra-acetic acid) can overcome these. Even so under certain circumstances of high aluminium its effectiveness, and the effect of ionic strength is questioned[20]. In Chapter 4.6. a considerable discrepancy was seen in the observed as against the expected concentration of fluoride in the loch water and it seems likely that the apparent fluoride concentration in the leachate is a gross under-estimate.

9.1.2.3. GRAVIMETRIC AND TITRIMETRIC DETERMINATIONS.

Alkalinity[166]. Alkalinity was determined by titrating the sample against a standardised 0.05 M sulphuric acid solution to pH 4.5. The sample must be stirred and the titration carried out slowly enough for carbon dioxide to be released from solution. For the determination of alkalinity in the leachate it was necessary, after

recording the pH, to dilute the sample to 1/10 strength prior to titration. Alkalinity is conservrd and so the alkalinity of the leachate is given by multiplying the recorded figure by 10.

Suspended Solids and Ash[167]. This procedure involves the removal of suspended matter from the sample onto a pre-washed, pre-weighed glass fibre disc (grade C) by vacuum filtration with subsequent drying at 105°C and reweighing. The disc must be wetted with water prior to addition of the sample. A modification was applied to analysis of the leachate whereby the sample was filtered through two discs instead of one. The result for dissolved solids retained by the lower disc was subtracted from that for the upper disc in order to obtain the result for suspended matter only. It is essential with high dissolved solids samples to pre-wet the glass-fibre thoroughly, in which case it is found that the uptake of dissolved salts is adequately limited. For the determination of ashed suspended solids the suspended solids were filtered onto pre-ignited and pre-washed and weighed discs. After determining suspended solids the discs were ignited at 500°C for the determination of ash.

9.1.2.4. MANUAL SPECTROPHOTOMETRIC DETERMINATIONS.

Sulphide[164]. A fixed sub-sample prepared as described under Chapter 9.1.1.1 was allowed to settle and the clear aqueous phase carefully removed with a Pasteur pipette. The bottle was filled with water, stoppered, inverted several times and settled. The aqueous phase was again removed and the sample made to 100 cm^3 with water. The bottle was inverted several times to disperse the suspension. Aliquots (either 5 cm^3 or 20 cm^3 depending on expected concentration) were taken and determined by the formation of methylene blue which was

measured spectrophotometrically. During mid-1984 the procedure was modified to use the DPD (ethylene blue) method[156] which is considerably more sensitive. This method was used for the analysis of all interstitial waters. Zinc (at >0.5%) suppresses response at low levels of sulphide and it is important to use the correct quantity of sodium carbonate during fixing and to wash the precipitate as described.

Chlorophyll-a[157]. Replicate samples and blanks were pre-treated and preserved as described in Chapter 9.1.1.1. Each sample consisted of a small amount of solid removed on station by filtration onto a membrane buffered with magnesium carbonate, and steeped in acetone in a screw cap tube. The tubes were retained at 4°C wrapped in aluminium foil for 24 hours prior to analysis. The acetone extract was made to 15 cm^3 and the solids removed by use of a centrifuge. The determination procedure contained in the reference was followed.

Due to the three dimensional spatial distribution of plankton in the loch it is evident that a sample taken from the outlet area at a single depth is grossly inadequate. However, it was not possible, given the timescale and pressure of work, to present anything more than a cursory indication of the state of phytoplanktonic activity in the loch at any one time.

9.1.2.5. AIR SEGMENTED CONTINOUS FLOW AUTOMATIC ANALYSIS WITH PHOTOMETRIC DETECTION.

The principle of this operation is covered by an essay review by the Standing Committee of Analysts (DOE/NWC)[168]. The laboratory of the FRPB in which these determinations were performed uses a Technicon

AutoAnalyzer II system.

Following the pre-analysis preparation of samples from this study, samples were, as far as possible, incorporated into the normal workload operation of the instrument. Results were entered to the computer archive system by the analyst; whose valuable assistance is greatly appreciated.

Oxidised nitrogen[169]. Nitrite was determined by diazotisation and coupling with sulphanilamide. Nitrate was automatically reduced to nitrite by hydrazine-copper reagent prior to diazotisation and the nitrate result obtained by difference.

Ammoniacal nitrogen[170]. Ammonia was reacted with sodium hypochlorite to form monochloramine which reacts with phenol and sodium nitroprusside to form indophenol-blue which was determined colorimetrically.

Chloride[171]. Chloride releases thiocyanate ion from its mercury(II) salt which forms a red compound with iron(III). Thus colorimetric determination of the iron(III) thiocyanate is directly proportional to chloride content.

Silica[172] and orthophosphate[173] were determined by procedures generating silico- and phosphoromolybdenum blue respectively. Only "molybdenum reactive" silca is determined - this being monomeric, dimeric and to some extent lower polymeric silicic acid and silicates.

Boron[174]. Boron was determined by the colorimetric measurement of a yellow complex formed by the reaction with azomethine-H [a condensation product of H-acid (8-aminonapth-1-ol-3,6-disulphonic acid monosodium salt) and salicylaldehyde]. Background correction for sample colour was essential.

Sulphate[175]. Dissolved sulphate was precipitated by 2-aminoperimide and the excess reagent dialysed and measured at 520nm.

9.1.2.6. ATOMIC ABSORPTION SPECTROPHOTOMETRIC DETERMINATION.

AAS is a standard technique for the analysis of metals and its principle of operation is covered in an essay on the subject issued by HMSO[176]. All the determinations undertaken were performed on an Instrumentation Laboratories IL357 equipped with IL254 autosampler except for Al and As which were determined on an IL151. Some trace metal analyses performed after mid-1984 were carried out using an IL Video 11 instrument. Prior to mid-1983 Mn, Cu, Cr, Cd, Ni, Pb and Zn were determined by flame atomisation on solutions concentrated 10x by evaporation. Between mid-1983 and mid-1984 Cd and Pb were determined by electrothermal means using a IL655 furnace atomisation accessory and after this date all these trace metals, and Al at trace level, were determined by a similar process without pre-concentration. Prior to mid-1984 background correction was by means of a deuterium arc lamp after which time Smith-Hieftje correction was employed. A consideration of these techniques is given by Sotera & Kahn[177], obtainable through Instrumentation Laboratories.

Following the pre-analysis preparation, samples for Ca, Mg, Na, K, Fe and As were, as far as possible, incorporated into the normal

workload operation of the instrument. Results were entered to the computer archive system by the analyst whose valuable assistance is greatly appreciated.

Table 9.1 sets out conditions for the determination of the metals concerned. Further details are contained in the working manuals for the instruments and also (for flame atomisation) through HMSO for Ca^{178}, Mg^{179}, Na^{180}, K^{181}, Fe and Mn^{182}.

Element	Digestion technique	Pre-treat.	Wavelength (nm)	Mode	Comment
Ca	1%HCl	1% La	422.7	AA-Ab	
Mg	ditto	1% La	202.5	AA-Ab	
Na	ditto	none	330.2	AA-Ab	dilute leachate
K	ditto	none	766.5	AA-Em	
Fe	4%HCl+boil	none	248.3	AA-Ab	
Mn	2%HNO_3+boil+ 10xconcentrate	none	279.5	AA-Ab-B	
Cu	ditto	none	324.7	AA-Ab-B	
Cr	ditto	none	357.9	AA-Ab-B	
Ni	ditto	none	232.0	AA-Ab-B	
Zn	ditto	none	213.9	AA-Ab-B	
Mn	2%HNO_3+boil	none	279.5	EA-Ab-B	
Cu	ditto	none	324.7	EA-Ab-B	
Cr	ditto	none	357.9	EA-Ab-B	
Ni	ditto	none	232.0	EA-Ab-B	
Cd	ditto	none	228.8	EA-Ab-B	
Pb	ditto	.05%La	217.0	EA-Ab-B	
V	4%HCl+boil	to 100ppm Al	318.5	AA-Ab-B	
Al	ditto	none	309.3	NA-Ab-B	dilute leachate
As	2%HCl+boil	reduce As(V)	193.7	HG-Ab-B	dilute leachate

TABLE 9.1. Conditions for AAS determination of metals.
AA= air acetylene flame, NA= nitous oxide acetylene flame,
HG= hydride generation with argon hydrogen flame,
EA= electrothermal atomisation, Ab= absorption, Em= emission,
B = background correction

9.1.3. STATISTICAL APPRAISAL OF ANALYTICAL PROCEDURES.

Table 9.2 presents information of the performance of these methodologies. Data is taken from quality control within the analysing

Parameter	Sample conc'n	standard deviation	limit of detection	units	notes
oxygen	all	0.05-0.1	0.2	mg/l	(a)
BOD	to 6	0.25	0.5	mg/l	(b)
pH	4-11	0.02-0.05	---		(b)
F	0.1	.001-.006	0.01	mg/l	(a)
	5	.027-.16			
alkalinity	424	1.1	5	mg/l	(a)(b)
	1060	2.1		$CaCO_3$	
susp.solids	43	2.8	2.5	mg/l	(a)(b)100 cm3 sample
ash	14	0.2-1.4	2.5	mg/l	(a)(b)100 cm^3 sample
sulphide			0.5	mg/l	(b) by methylene blue
	0.05	0.0018	0.005	mg/l	(a) by DPD
chlorophyll			10	ug/l	(b)
nitrate	1	0.05	0.1	mg/lN	(b)
	9	0.15			
nitrite	0.1	0.01	0.01	mg/lN	(b)
	0.9	0.02			
ammonia	0.2	0.02	0.04	mg/lN	(b)
	1.8	0.06			
chloride	20	0.7	1	mg/l	(b)
	180	1.6			
silica	1	0.06	0.1	mg/l	(b)
	8	0.07		SiO_2	
borate	0.1-1	0.02	0.04	mg/lB	(a)(b)
	4	0.04			
sulphate	23	0.67	2	mg/lS	(b)
	46	0.76			
aluminium			0.5	mg/l	(b)(c)(d)
arsenic				not available	
cadmium			0.005	mg/l	(c)(d)
calcium			0.005	mg/l	(c)
chromium			0.03	mg/l	(c)(d)
copper			0.01	mg/l	(c)(d)
iron			0.01	mg/l	(c)
lead			0.05	mg/l	(c)(d)
magnesium			<0.002	mg/l	(c)
manganese			0.005	mg/l	(c)(d)
nickel			0.02	mg/l	(c)(d)
potassium			0.004	mg/l	(c)
sodium			1	mg/l	(c)(insensitive w.l.)
vanadium			0.3	mg/l	(c)
zinc			0.005	mg/l	(c)

TABLE 9.2. Analysis of Aqueous Samples - Statistical Performance of Analytical Procedures. (a) see main reference under determinand (Chapter 5.1.2), (b) data from analysing laboratory, (c) data for flame atomisation see reference 176, (d) data for electrothermal atomisation not available but known to be 1000x more sensitive or better.

laboratory, from the main references in the sections above, or from other specified sources. Standard deviation is, wherever possible, given as the total standard deviation on a single result and limit of detection is given by 4.65_{Sw}, where $_{Sw}$ is the within batch standard deviation[160].

9.2. CHEMICAL ANALYSIS OF SEDIMENT SAMPLES

9.2.1. X-RAY FLUORESCENCE SPECTROMETRY.

A Phillips PW 1450 sequential automatic X-ray Spectograph was employed for these analyses. For major and minor elements it was possible to use the autosampler tower but for the counting of membranes individual presentation of samples was required. Instrumental control was by means of an interfaced Apple microcomputer, and averaged count data was manipulated using programs within the Edinburgh Multiple Access System (EMAS). Minor element data was processed using programs developed for sediment studies by S Rainey and G Shimmield. Printout of averaged raw count rates was provided following membrane analysis and the processing of this data was carried out on the Data General Nova 3 system of the FRPB.

9.2.1.1. FUSED DISC PROCEDURE.

Fused glass discs (45 mm diameter) were prepared according to the procedure of Fitton et al[183], based on that of Norrish & Hutton[184]. Samples dried to constant weight at 70°C were used. The whole sample was ground in a tungsten carbide ball-mill for 2 minutes and an aliquot of approximately 1.3 g weighed accurately (to 0.001 g) into a 95%Pt:5%Au crucible with a Pt lid. The crucible and lid were ignited at 1100°C for 1 hour and allowed to cool. The crucible was reweighed and, if the ignited sample weight was below 0.9 g, more sample was

added and the ignition repeated. The initial and final weights were noted in order to allow later compensation for loss on ignition. Flux was added in the ratio 5:1 of sample plus an additional 0.03 g to allow for flux volatility. The flux used was Spectroflux 105 (Johnson-Matthey Chemicals Ltd.) consisting of $Li_2B_4O_2$, La_2O_3 and $LiCO_3$. The borate acts as a flux while La, being a heavy absorber of X-rays, helps to minimise matrix effects from samples of differing compositions. The crucible was returned to the muffle furnace for 20 minutes before being removed and allowed to cool. The crucible was reweighed and flux added so as to achieve a 5±0.005:1 flux:sample ratio. If it was necessary to add more than 0.05 g flux then the crucible was returned to the furnace for a further 20 minutes and the procedure repeated. The crucible, with lid, was placed over a Meker burner to re-fuse the sample. Meanwhile disc-casting equipment was kept at 220°C on a hotplate. The melt was poured onto a graphite mould inside a stainless steel cylinder and an aluminium plunger used to press the disc. This provided an "orange-peel" surface to the disc for presentation to the X-ray beam. The disc and mould were covered with a silica crucible and retained at 220°C for 30 minutes before being allowed to cool.

International rock and sediment standards were used for calibration of the response of the elements. The standards used are listed in Table 9.3 and details of instrument settings in Table 9.4. A statistical appraisal of the method has been taken from Fitton et al[183] and are included in Table 9.5. Precision was checked by means of discs prepared from a single sample (2 degrees of freedom) and found to be satisfactory. I am grateful to G Fitton and D James for

their kind assistance and to D James for carrying out the XRF analysis and data manipulation on my behalf. Data manipulation involved calibration of elemental response and an iterative procedure for the correction of results for matrix interferences.

It is recognised that Na, K, and to an extent Mg may be lost as volatile salts, principally chloride, during the ignition stage. Chloride may also be lost by generation of hydrogen chloride by reaction with significant levels of organic matter. Although it is not possible to quantify the losses, they should not be significant in the context of the present study where chloride levels are not high, and in themselves are not of particular importance.

9.2.1.2. PRESSED POWDER PROCEDURE

Minor element analysis was carried out on 45 mm pressed pellets using a modified procedure based on that of Fitton et al[183]. Freeze-dried sample was used for this process. The whole sample was ground in a tungsten carbide ball-mill for 2 minutes prior to use. Approximately 5 g was placed in the stainless steel mould assembly and compacted with a perspex plunger which was then removed very carefully, along with the inner guide cylinder of the mould. Binding compound was not used as binder tends to raise salts to the surface of a pellet made from sediments. Two teaspoonfuls of sieved boric acid was carefully placed around and over the pellet and after insertion of the stainless steel plunger, a load of 10 tonnes was applied for 1 minute. The pressed pellet with its boric acid backing was then presented to the X-ray beam, for analysis within 8 hours of preparation.

Operating conditions are contained in Table 9.4 while a statistical

appraisal is included in Table 9.5 (after Shimmield[26]). These precision data were based on work carried out using a Tungsten target X-ray tube as source, whereas present analysis employed a Rhodium target tube. However within a limited number of degrees of freedom used for appraisal the differences should not be significant, and compare favourably with precision check by means of pellets prepared from the same sample (2 degrees of freedom). Calibration was by means of international standard rock and sediment pellets counted within the batch. Additionally, for minor elements not satisfactorily covered by such standards, standards were available that had been prepared by dilution series spiking of standard sediment with minor elements and were previously used by G. Shimmield[26]. Table 9.3 lists the standards employed. Averaged (peak-background) data, taken from the Apple microcomputer, were manipulated on EMAS in two stages. Data were corrected for major element composition (available for standards and samples) using theoretical mass absorption coefficients and again similarly for the minor elements so calculated. Interference corrections were applied for Ti on V, V on Cr, Rb on Y and Sr on Zr. Calibration graphs were prepared of count data for selected standards against known concentrations of minor elements so that a final presentation of concentration was possible. I am grateful to G. Shimmield for his kind assistance and advice with this work.

9.2.1.3. THIN-FILM PROCEDURE.

The analysis of a very thin film of particulate matter by XRF allows major component elements to be determined on extremely small samples. The theory of this procedure has been covered by Liebhafsky *et al*[185] and its application to suspended matter in water by Cann and

Major element analysis (fused discs)	Minor element analysis (pressed pellets)		
AGV1	AGV1	GSP1	MA3
ANG	BCR1	BLANK	MA4
BCR1	BCSS1	I1 (i)	MA5
BEN	BP1 (b)	I2	MAG1
BR	BP2	I3	MESS1
DTS1	BP3	I4	PCC1
G2	BP4	I5	S1
GA	BP5	I6	S2
GH	BR	JB1	SCO1
GSP1	G2	JG1	SGR1
MAN	GA	MA1 (a)	SY2
PCC1	GH	MA2	SY3
			W1

TABLE 9.3. International rock and sediment samples used as standards for fused disc and pressed pellet procedures. Synthetic dilution series are marked (a) containing MoO_3 and As_2O_3 in sediment matrix, (b) containing NaBr in similar, (i) containing $Ba(IO_3)_2$ in chalk matrix (labelled BLANK).

Winter[186]. Several workers have applied the technique to the analysis of particles suspended in sea water, including Baker and Piper[187] and Ridgway[188]. A very small amount of finely ground sample is applied to a polycarbonate or ion exchange membrane so that no more than 100 ug is applied, forming a layer of the order of 10 um in thickness. If this requirement is not exceeded then the elements Na, Mg, Al, Si, K, Ca, Ti, Mn, and Fe may be determined without the need for matrix correction due to mass absorption. The procedure is evidently open to contamination from the atmosphere and matter suspended in reagents. Consequently great care must be taken by filtering all distilled water and reagents through a 0.45 um polycarbonate membrane and by using only scrupulously cleaned apparatus held in polythene bags when not in immediate use. Exposure to the atmosphere of any apparatus or solution should be kept to a minimum.

Element	Sample	Line	Tube	kV	mA	Peak 2θ	Backgd 2θ	Pulse ht. LL	Pulse ht. Win.	Instrument Conditions
Al	Fd	Kα	Cr	50	45	144.78	139.01	250	600	PE F c
As	Pp	Kβ1	Rh	90	30	30.48	31.20	200	600	LF FS f
Ba	Pp	Lβ2	Rh	60	45	115.44	117.74	300	500	LF FS c
Br	Pp	Kα	Rh	90	30	29.98	28.60	200	600	LF FS f
Ca	Fd	Kα	Cr	50	30	113.09	110.00	200	600	LF F f
Cl	Pp	Kα	W	90	30	66.51	66.60	200	600	PE F c
Cr	Pp	Kα	Rh	60	45	69.37	70.81	150	600	LF F f
Cu	Pp	Kα	Rh	60	45	45.11	46.61	150	600	LF F c
Fe	Fd	Kα	Cr	50	45	57.52	55.81	150	700	LF F f
I	Pp	Lα1	Rh	60	45	102.88	103.80	300	500	LF FS f
K	Fd	Kα	Cr	50	45	136.63	131.78	200	600	LF F f
Mg	Fd	Kα	Cr	50	45	45.26	43.28	200	600	TL F c
Mn	Fd	Kα	Cr	50	45	62.98	62.08	150	600	LF F f
Mo	Pp	Kα	Rh	90	30	20.28	20.70	200	600	LF S f
Na	Fd	Kα	Cr	50	45	55.22	53.22	250	500	TL F c
Ni	Pp	Kα	Rh	60	45	48.66	49.99	150	600	LF F f
P	Fd	Kα	Cr	50	45	141.07	144.27	330	400	GE F c
Pb	Pp	Lβ2	Rh	90	30	28.23	29.30	250	500	LF FS f
Rb	Pp	Kα	Rh	90	30	26.58	25.76	250	600	LF FS f
S	Pp	Kα	Rh	60	45	110.72	111.30	250	500	GE F c
Si	Fd	Kα	Cr	50	45	109.04	115.49	250	600	PE F c
Sr	Pp	Kα	Rh	90	30	25.11	24.24	250	600	LF FS f
Ti	Fd	Kα	Cr	50	45	86.14	90.80	250	600	LF F f
Th	Pp	Lα1	Rh	90	30	27.45	27.95	250	500	LF FS f
V	Pp	Kα	Rh	60	45	123.40	120.78	300	500	LF F c
Y	Pp	Kα	Rh	90	30	23.76	24.35	250	600	LF FS f
Zn	Pp	Kα	Rh	60	45	41.77	40.97	250	500	LF FS f
Zr	Pp	Kα	Rh	90	30	22.51	22.95	250	600	LF FS f

TABLE 9.4. Analytical conditions for XRF major and minor elements.
LL = lower level, Wind. = window
Sample : Pp = pressed pellet, Fd = fused disc,
Crystal : LF = LiF200, TL = Thallium acid phthalate,
: Ge = Germanium, PE = Pentaerythritol,
Counter : F = flow, FS = flow+scintillation, S = scintillation,
Collinator: f = fine, c = coarse

element %	mean	s.d.	element %	mean	s.d.
SiO_2	43.8	0.09	Na_2O	3.610	0.040
Al_2O_3	14.06	0.05	K_2O	1.412	0.005
Fe_2O_3	12.46	0.03	TiO_2	3.165	0.006
MgO	8.31	0.03	MnO	0.215	0.007
CaO	10.62	0.03	P_2O_5	1.030	0.003

element p.p.m.	mean	% var.	LOD	element p.p.m.	mean	% var.	LOD
As	11	6.90	0.20	Rb	80	4.53	2.24
Ba	330	3.10	5.05	S	4600	1.94	67.81
Cl	31200	0.40	49.3	Sr	156	3.18	3.35
Cr	105	2.20	1.72	Th	13	28.72	0.40
Cu	30	2.79	0.58	V	140	1.76	1.29
I	100	1.87	1.40	Y	35	6.70	0.68
Mo	2	16.25	0.08	Zn	120	2.98	2.23
Ni	54	4.19	1.53	Zr	130	3.63	2.42
Pb	23	20.88	0.72				

TABLE 9.5. Statistical appraisal of analytical methods by XRF. Major elements are after Godfrey et al with 4 degrees of freedom. Minor elements are after Shimmield where
LOD = $3/c \times \sqrt{Rb/Tb}$ and % var. = $100/\sqrt{Tp} \times 1/\sqrt{Rp-\sqrt{Rb}}$
where c=counts/s/%, Rb=backgd. count rate, Tb= time on backgd., Rp=peak rate count and Tp=time on peak.

Samples used for this analysis were ground using a agate mortar and pestle for a period of at least 30 minutes (unless stated otherwise). Approximately 10 mg was accurately weighed into a 5 cm^3 weighing jar and 3 cm^3 distilled water added. The jar was placed in an ultrasonic bath and agitated for 30 minutes. The contents were transferred to a 100 cm^3 volumetric flask, ensuring complete transfer by ultrasonic vibration of each of three rinses of the jar which were then poured into the flask. The contents of the flask were made to approximately 60 cm^3 with water and thoroughly shaken. The flask was ultrasonically agitated for 60 minutes, being removed each 20 minutes and thoroughly shaken for 2 minutes. The contents were transferred to a 1 l volumetric flask, and each of three rinses being vibrated for 10 minutes prior to transfer. The contents were made to 1 l and vigorously shaken for 2 minutes. Figure 9.3 illustrates the perspex

filtration apparatus that was used.

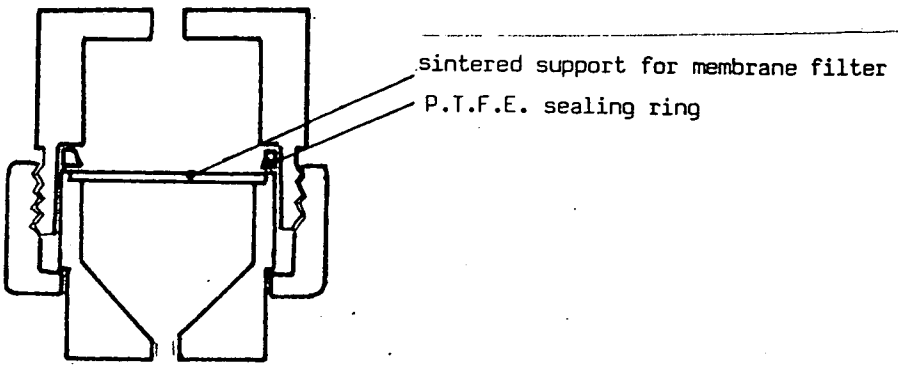


FIGURE 9.3. Membrane Filtration Apparatus.

A 37 mm diameter 0.45 um clear polycarbonate membrane was loaded with tweezers onto the sinter and the filter top, complete with 'O' ring secured. The flask was completely inverted 10 times and 10 cm^3 immediately taken from the centre of the suspension using a bulb pipette. The suspension was released into the filter assembly. A vacuum was applied for exactly 30 s. This was found to give more even coverage than continuous application of vacuum. The filter was disassembled and the membrane placed in a covered perspex petri dish. The lid of the dish was cracked open and dried in an oven at 30°C for 2 hours. Five replicates of each sample were prepared.

Membranes so prepared were subjected to various treatments as described in the appropriate section (ensuring 5 replicate membranes for each sample and treatment). Previous workers have found that particles cannot be washed from the membrane (N.B.Price, personal communication) and that the membrane is not damaged by reagent treatment (Ridgway[188]). Blank membranes were prepared for each preparation used.

Operating conditions for the XRF are included in Table 9.6.

Element	Count	Line	Tube	kV	mA	Peak 2θ	Backgd 2θ	Pulse ht. LL	Win.	Instrument Conditions		
Al	2E5	Kα	Rh	40	60	144.95	139.18	250	600	PE	F	c
Ca	4E5	Kα	Rh	50	45	113.23	109.73	250	600	LF	F	c
Fe	2E5	Kα	Rh	50	45	57.54	55.83	200	600	LF	F	f
K	4E5	Kα	Rh	50	45	136.80	131.78	200	600	LF	F	c
Mg	2E5	Kα	Rh	40	60	45.30	47.80	250	500	TL	F	c
Mn	2E4	Kα	Rh	50	45	63.01	62.11	150	700	LF	F	f
Na	2E4	Kα	Rh	40	60	55.25	53.25	250	500	TL	F	c
P	4E4	Kα	Rh	40	60	141.07	144.27	330	400	GE	F	c
Si	4E5	Kα	Rh	40	60	109.16	113.66	250	600	PE	F	c
Ti	2E5	Kα	Rh	50	45	86.15	90.81	300	500	LF	F	f

TABLE 9.6. Conditions for XRF Thin-Film Analysis.
LL = lower level, Wind. = window, Crystal : LF = LiF200, TL = TLAP,
Counter : F = flow, Collinator: f = fine, c = coarse
Count : eg. 2E5 = 2×10^5 counts.

Calibration was achieved by analysing samples taken from the cruise of R/V Thompson in 1979, for North Pacific Stations 2 to 15. These samples were of known elemental composition and kindly supplied by N.B.Price. Analytical result summaries were studied and a total of 15 samples, which provided a range of elemental concentrations suitable for calibration at levels expected during the present studies, were chosen as standards. Table 9.7 tabulates the elemental masses reported for these (standard) membranes.

Figure 9.4 sets out the calibration curves obtained for single analyses of each of these standards. The calibration standards were backed by a different batch of membranes to those of the analysed samples and adjustment was necessary to allow for background levels of the elements in both batches of membranes. Additionally some allowance was necessary for the geometry of each sample turret since each of the three positions gave a slightly different presentation of membrane to the X-ray beam. This allowance, normalised to turret

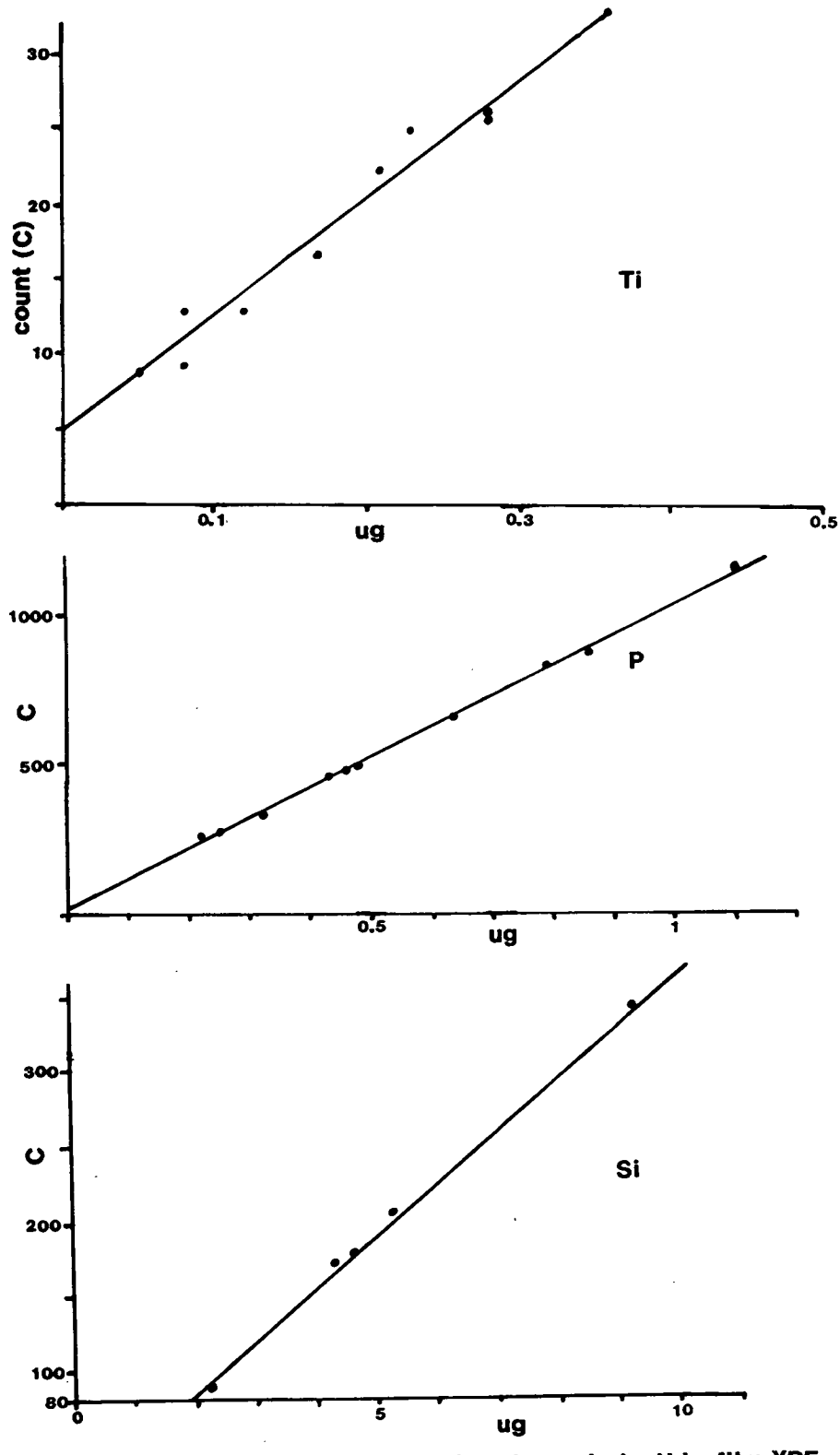
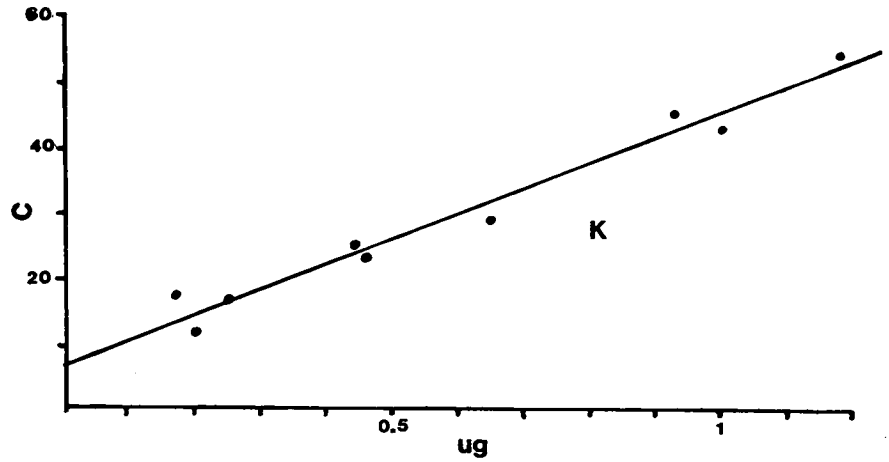
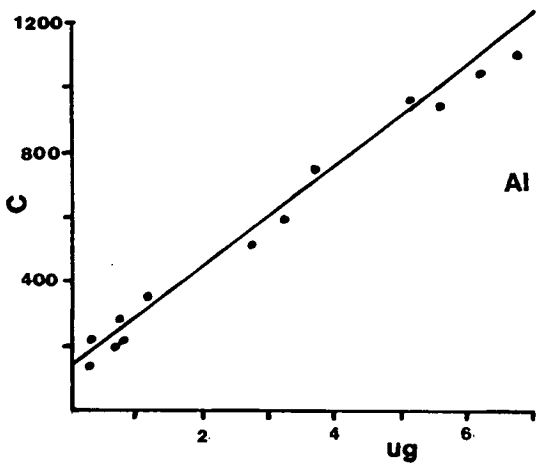
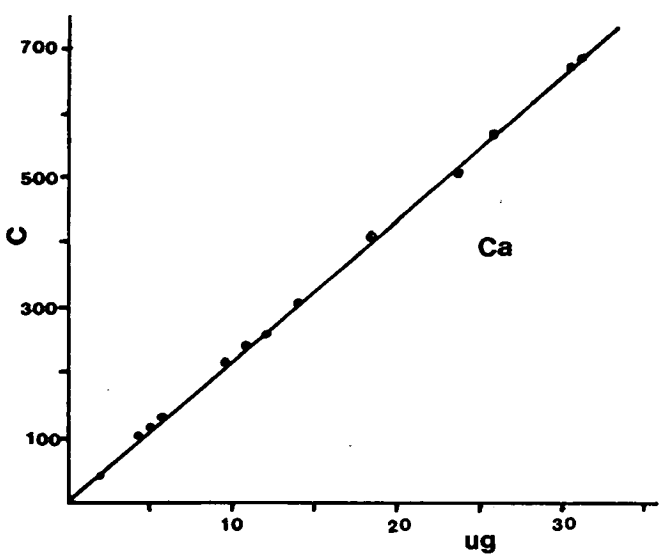
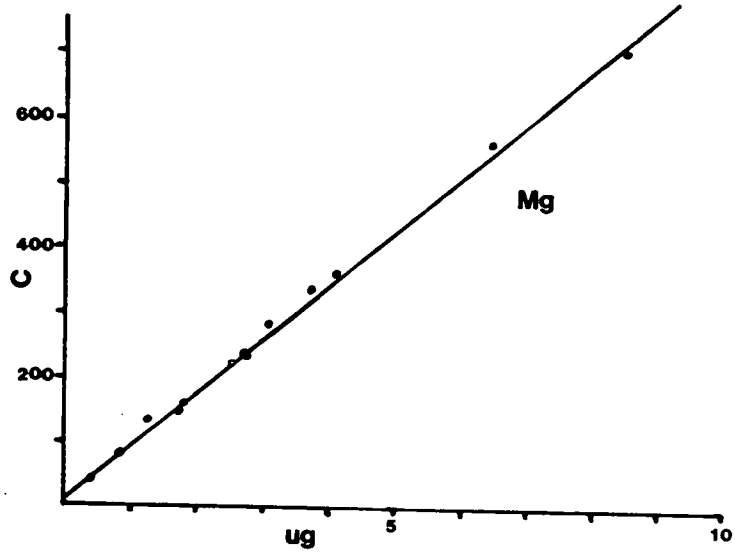


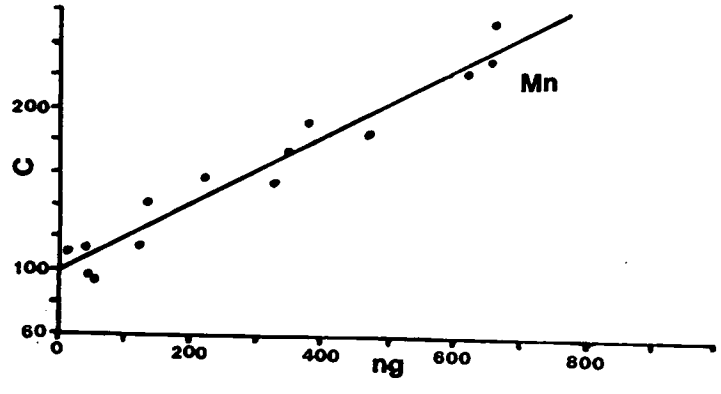
FIGURE 9.4. Calibration graphs for elements by thin-film XRF.

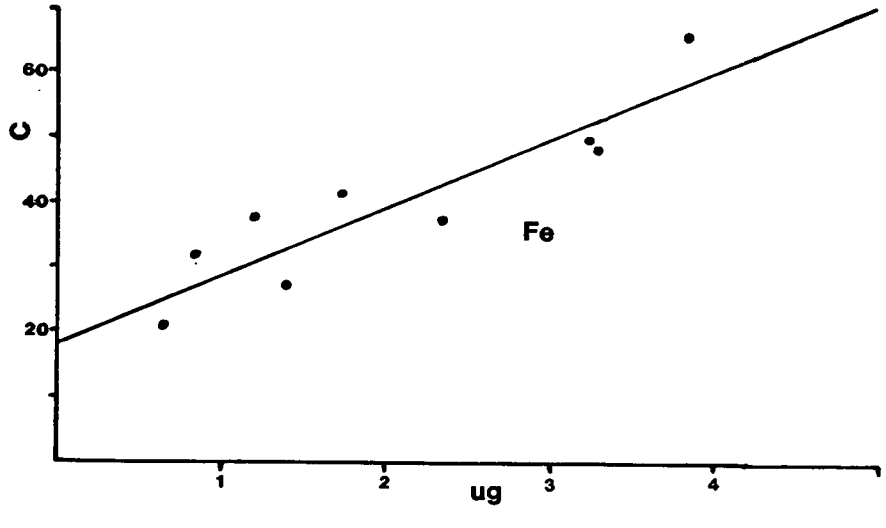

60
40
20
C
K
0.5
1
ug


1200
800
400
C
Al
2
4
6
ug


700
500
300
100
C
Ca
10
20
30
ug


600
400
C
200
Mg
ug
5
10


200
C
100
60
Mn
0
200
400
ng
600
800


60
C
40
20
Fe
1
2
ug
3
4

Sample	Cruise Stat'n	Al	Ca	Fe	K	Mg	Mn	P	Si	Ti
R36	2	0.75	11.9	2.35	0.46	1.75	58.9	0.46	4.57	0.12
R56	4	0.65	1.89	1.41	0.20	0.40	39.3	0.25	2.24	0.08
S51	5	0.29	4.39	0.85	0.17	1.27	45.6	1.46	4.29	0.05
S73	6	5.57	5.07	5.73	1.28	2.71	653	0.48	17.6	0.29
S75	6	2.28	13.2	3.11	3.12	10.2	254	0.51	10.6	0.15
S84	6	3.71	18.4	3.84	0.93	2.54	377	0.63	18.0	0.21
S86	6	1.15	5.60	1.20	0.25	0.84	136	0.22	5.28	0.07
S87	6	2.78	14.1	3.29	1.00	2.77	327	0.43	14.4	0.23
S90	6	6.74	30.4	5.24	1.36	4.12	219	1.10	29.5	0.29
S95	6	0.29	23.5	0.66	0.65	2.77	13.4	2.39	9.27	0.05
S96	6	0.73	31.2	1.73	0.44	1.77	126	1.56	13.9	0.08
T2	6	5.11	21.4	5.40	1.18	3.07	470	0.79	24.1	0.29
T3	6	6.18	25.8	5.62	1.41	3.70	346	0.86	27.2	0.37
T11	7	3.24	9.45	3.25	2.79	8.54	658	0.32	12.8	0.17
T63	15	28.2	10.8	16.6	3.79	6.43	616	1.93	82.9	0.96

TABLE 9.7. Elemental Mass on Membrane Standards.
All figure are ug on membrane except Mn in ng.

position 2 was, in practice insignificant relative to other sources of error. Thus for a count (C) to be directly read from the calibration graph for that element, the observed sample count (C_o) was first adjusted by

$$C = C_o - C_b + C_i$$

where C_b = observed blank membrane count and

C_i = count intercept from calibration graph (at mass=0ug)

Table 9.8 tabulates the standard deviations found for multiple replicate analysis of samples prepared during this study.

element	concentration (ug)	standard deviation (%)	element	concentration (ug)	standard deviation (%)
Si	2.3	10	Al	3.8	10
Fe	1.8	24	Mg	2.9	4
Ca	3.3	10	K	0.15	33
P	0.57	10	Ti	0.05	10

TABLE 9.8. Precision Obtained by Thin-Film XRF Analysis.

I am grateful to N.B.Price for his kind assistance and advice during this work.

9.3. C-H-N ELEMENTAL ANALYSIS.

A variety of methods have been used in determining the organic carbon content of sediment. Byers et al[189] spiked sediment with N-acetyl glucosamine and investigated procedures for its quantitative recovery. They found that wet oxidation yeilded 77% of the added carbon while ignition at 475-500°C yeilded 100%. Pretreatment with acid to destroy carbonate-C led to negligible recovery of the spike. Dankers and Laane[190] reported that the calculation of organic carbon by weight loss on ignition led to gross over-estimation of up to 4x in clayey sediments. Parker[191] in a study of the destruction of organic carbon by heating concluded that the results obtained by various workers using a variety of temperatures between 450 and 700°C could not be readily compared. Organic matter becomes more refractory as decomposition progresses and, although for most organic matter the greatest loss occurs at 200-300°C with little loss occuring above 500°C, for some aerobically digested materials the bulk of the carbon may be released between 500-600°C. In this study ignition at 475°C was employed (as preferred by Byers et al[189]).

Samples dried to constant weight at 70°C were used for the determination of carbon, hydrogen and nitrogen. The samples were ground in a ball mill prior to use. A sample was first subjected to analysis without pre-treatment in order to determine the concentration of the total elements. 100 mg was weighed into a small cup made from a 25 mm square of aluminium foil formed with the bottom of a test-tube. A number of these cups were placed inside a loose fold of aluminium

foil and placed in a muffle furnace at 475°C for 4 hours. The cups were reweighed and the loss on ignition calculated. An aliquot was subjected to analysis.

A Perkin Elmer Model 240 Elemental Analyzer was used by the kind permission of D.McLusky of the University of Stirling Department of Biological Sciences. A 30 mg aliquot of sample was loaded into a Pt boat and passed inside an oxidation furnace at 950-1000°C. The gases formed were swept by helium through a copper reducing furnace at 650-700°C and thence to a series of thermal conductivity detectors to determine carbon, hydrogen and nitrogen seperately. The analysis was calibrated by an acetanilide standard.

The determination of organic and inorganic carbon was then found according to the formula:

$$C_I = C_2(1-L/100)$$

and $$C_O = C_1 - C_I$$

where C_I = inorganic carbon
C_O = organic carbon
C_1 = total carbon
C_2 = ashed carbon (not corrected for L)
L = loss on ignition
where all parameters are measured in %

Nitrogen may be similarly divided into a volatile component (including organic nitrogen) and a refractory component. Hydrogen may be divided into a volatile fraction consisting of organic hydrogen plus some of the clay and hydrated iron mineral water, and that that is volatile between 475 and 1000°C comprising further water held in clay minerals. The samples will contain components originally dissolved in the interstitial water. However this contribution will be negligible even in very wet sediments (<0.02%).

Several samples were analysed in replicate to give the statistical appraisal found in Table 9.9.

element	concentration (%)	standard deviation	limit of detection
C	8.19	0.748	?
	2.06	0.102	
N	0.652	0.064	0.08
	0.017	0.017	
H	1.56	0.038	<0.1
	0.408	0.039	

TABLE 9.9. Statistical Appraisal of C-H-N Analyzer.
(4 degrees of freedom)

9.4. PARTICLE SIZE ANALYSIS OF SEDIMENT SAMPLES

APPARATUS (4 analyses).

4 x 63 um sieves and sieve receivers
4 x pneumatic troughs
1 set of sieve comprising 5.6 mm, 2 mm, 1mm, 500 um, 250 um, 125 um, sieve shaker and camel hair brush.
2 sets of 20 x 50 cm^3 beakers
4 x 1 l stoppered measuring cylinders (marked in cm from lip)
2 x 50 cm^3 pipettes (jet cut to 2 mm i.d. and marked at 100 mm and 200 mm from the tip)
4 x evapoating basins
4 x watch glasses
1 x 400 cm^3 beaker
1 x 0-50^oC thermometer
1 x stopwatch
2 x drying oven set at 70^oC and 95^oC respectively
box of 50 cm^3 plastic specimen jars

METHODOLOGY

300 cm^3 of well mixed, kneaded sample was placed in a 63 um sieve in a trough and 600 cm^3 of distilled water added. The sample was rubbed and puddled through the sieve until apparently complete and the water thoroughly drained into the trough. The covered sieve in its receiver was dried at 70^oC in an oven. The covered trough was maintained at 4^o C until dry sieving was complete.

After drying, the material on the sieve was thoroughly brushed through with a clean camel hair brush and the material transferred to the 500 um sieve. The bank of sieves ranging from 500 um to 63 um with receiver beneath was shaken in the sieve shaker for 15 minutes. Each sieve was brushed through and the bank shaken for a further 5 minutes. Each fraction was transferred to a weighed plastic specimen jar and reweighed to assertain fraction weight. However if the 500 um fraction contained a significant amount of material then the above procedure was repeated with 5.6 mm, 2 mm, 1 mm and 500 um sieves.

The material in the receiver was brushed to a fine powder and slowly added, with thorough agitation to the water in the trough. The slurry in the trough was allowed to reach ambient temperature. The slurry was thoroughly mixed before being transferred to a 1 l measuring cylinder. The trough was washed several times with 20 cm^3 of distilled water to ensure complete transfer and the washings added to the cylinder. The volume was made to 1 l with distilled water. The cylinder was inverted several times and then allowed to settle for the required time as shown in Table 9.10. depending on ambient temperature.

phi	5	6	7	8	9
depth (cm)	20	10	10	10	10
temperature (^{o} C)	time (s)	time (s)	time (s)	time (s)	time (s)
19	58	117	475	1883	7563
20	57	114	459	1835	7353
21	56	111	446	1789	7143
22	54	109	437	1745	6993

TABLE 9.10. Settlement Times for Fractions at Ambient Temperatures.

A pipette was lowered to the required depth and 50 cm^3 of suspension withdrawn and immediately transferred to a weighed beaker. The outside of the pipette was wiped with a tissue and the inside flushed with water, which was added to the beaker. The beaker was placed in an oven at 70°C. The cylinder was inverted several times and then settled for the next time interval until 5 samples had been taken and transferred to beakers for evaporation to dryness. On dryness the beakers were reweighed to obtain the weights of sample present at and below that particular size and transferred to plastic specimen jars. Note that dry sieve weights were the true weights in that fraction whereas pipetted weights required subtraction from the next size down in order to obtain fractional weight.

APPENDICES

APPENDIX A

RESULTS OF CHEMICAL ANALYSIS OF WATER FROM KINGHORN LOCH AND ASSOCIATED INPUTS

A.1. DATA HANDLING AND PRESENTATION OF STATISTICS

Routine chemical data derived from aqueous samples taken during this study are held on the Data General Nova 3 computer system of the F.R.P.B. The data are held within the chemical archive system of the Board and are contained by the river catchment area 3. The data are indexed by the code, unique to each sampling station, shown below:

Sampling station	Code
North inlet to Kinghorn Loch (at Craigencalt Farm)	28
Kinghorn Loch at outlet sluice	304
Leachate to Kinghorn Loch (at roadside dam)	305
Kinghorn Loch (water body stations)	308

Data are currently held in ASCII format, sample by sample and readily retrievable by the input of the code for that station. The computer program "KLOCHPRINT" collects data from the archive and assembles individual binary matrix files in sample order ready for manipulation. "KLOCHPRINT.2" is automatically chained and rearranges the matrix into determinand order and extends it to include the statistical data. It then sequentially provides hard copy of the data determinand by determinand, until complete when it presents a statistical appraisal of concentration units followed by an appraisal of loadings.

The mean concentration and mean loading have been calculated as the arithmetic mean of individual concentration and loading data. Sampling frequency requirements have been calculated at 20% (column n20 on tables), 10% (column n10) and 5% (column n5) to indicate the number of samples that would be required to be taken for that

determinand at that station such that the mean would be within the stated percentage, at 95% confidence limit, of the true long-term mean. Standard deviation and sampling frequency calculations have assumed a near normal distribution so that the frequency required using unbiased data is described by

$$N=(t.s)/(f.m)$$

where N = required sampling frequency for fx100 precision
f = fractional precision required
t = students t for 95% confidence limit and N-1 degrees of freedom
s = standard deviation about the mean for single result
m = mean

f values required to satisfy 20%,10%, and 5% were normally 0.2, 0.1, and 0.05 respectively but for pH with a log relationship values approximated to 0.1, 0.05, and 0.02 respectively.

"KLOCHPRINT.2" uses a value of t=1.96. Evidently since t has N-1 degrees of freedom this value will underestimate N if N is small (by about 10% if N=20). However all important parameters (except chlorophyll-a, arsenic and vanadium) were analysed on at least 100 occasions during the relevant part of the study and if N is less than 100 then this over generous estimate of precision must be considered. At N=100 this estimate of t is reasonable.

A.2. STATISTICAL PERFORMANCE ACHIEVED

Hinchcliffe[192] collated data collected from 20 sampling points throughout England in an appraisal of sampling frequencies required for the Harmonised Monitoring Scheme of River Water Quality. The scheme applied a requirement of the mean being within 20% of the true average concentration and found that for important determinands a range of 7 to 32 samples were required with a mean of 16 samples. The present study proposed to use a 10% limit in order to provide a

reasonably accurate input into the speciation model of the loch. However only the north inlet managed to achieve this level of consistency while the outlet of the loch and leachate were more varied on some important determinands. However the weekly sampling interval achieved an estimate of required frequency that was generally satisfactory at the 10% requirement for all three stations for concentration though only at 20% for some loadings. Thus this intensity of sampling would appear satisfactory, though not generous, to allow a reasonable statement of the chemical composition of the inputs and the loch and for an understanding of the chemical processes involved. It must however question the reliability of input data to the mathematical model. Indeed, given this treatment of the data, it questions how reliable data normally is when used in computer simulation work.

A.3. COLLECTED DATA FOR AQUEOUS CHEMISTRY

The following tables will be found under this section:

1. Leachate to Kinghorn Loch from 4-1-1981 to 24-5-1983; including a statistical appraisal of concentration and loading.
2. North Inlet to Kinghorn Loch from 4-1-1981 to 24-5-1983; including a statistical appraisal of concentration and loading.
3. North Inlet to Kinghorn Loch from 30-5-1983 to 27-9-1984; including a statistical appraisal of concentration and loading.
4. West Inlet to Kinghorn Loch from 14-6-1983 to 27-9-1984; including a statistical appraisal of concentration and loading.
5. Kinghorn Loch at outlet from 4-1-1981 to 24-5-1983; including a statistical appraisal of concentration.

6. Kinghorn Loch at outlet from 30-5-1983 to 27-9-1984; without statistical appraisal.
7. Kinghorn Loch water body stations taken on 23-2-1981; including a statistical appraisal of concentration.
8. Kinghorn Loch water body stations taken on 1-7-1981; including a statistical appraisal of concentration.
9. Kinghorn Loch water body stations taken on 24-8-1981; including a statistical appraisal of concentration.
10. Kinghorn Loch water body stations taken on 5-10-1981; including a statistical appraisal of concentration.
11. Kinghorn Loch water body stations taken on 30-10-1981; including a statistical appraisal of concentration.

It was not felt appropriate to apply any statistical evaluation to Kinghorn Loch water after May 1983 as this was a period of rapid improvement.

The following abbreviations were applied to all tables:

abbreviation	meaning
tot	total concentration of determinand (includes that contained in suspended solids).
dis	concentration of determinand passing 0.1um membrane filter (except alkalinity which passes glass fibre disc grade C; 1um or better).
unspecified	for determinands normally considered to be completely soluble in water, concentration is that which passes glass fibre disc grade C.
alk	alkalinity to pH4.5.
EC	electrical conductivity(ambienttemperature c.21 ^{o}C)
...	not determined.

For Tables A.7 to A.11 sample headers represent the station designation (see Figure 4.1.) with the depth at which the sample was taken in parentheses where BOT-.5m indicates 0.5m from the sediment surface. Note that due to the variation in level of the loch surface the depth of water at any station may vary from survey to survey.

TABLE A.1. Chemical analysis of the leachate to Kinghorn Loch (taken at roadside dam) for the period 4-1-1981 to 24-5-1983; including statistical appraisal.

LEACHATE TO KINGHORN LOCH for 4/1/81 to 23/2/81

date	4/1/81	9/1/81	20/1/81	25/1/81	29/1/81	2/2/81	9/2/81	15/2/81	23/2/81	
time	1650	0930	1120	1230	0930	1120	1040	1755	1450	
flow	1	3	4.4	3	3.4	3	3.4	2.6	2.6	l/s
temp	4	6	3	4	5.5	7	4	5.5	4.5	C
pH	11.8	11.6	11.8	11.8	11	11.4	11.9	11.3	12	
tot Ca	14.1	21.3	4.1	12.5	16.5	...	8.7	13.6	6.9	mg/l
dis Ca	...	...	...	...	...	...	...	...	...	mg/l
tot Mg	8.6	11.2	12.6	13.3	12.1	...	14.4	14.9	15.6	mg/l
dis Mg	...	...	...	...	...	...	...	...	...	mg/l
Na	1660	1441.5	2150	1400	1250	...	1847	1204	1536	mg/l
K	27.7	28.4	21	18	14	...	25.5	20.5	23	mg/l
tot Al	159	125	192	92	63	66	139	66	106	mg/l
dis Al	154	60	173	84	59	50	...	...	...	mg/l
tot Fe	.4	.6	.5	.4	.1	...	...	...	...	mg/l
dis Fe	...	...	...	...	...	...	...	...	...	mg/l
tot As	2.06	1.48	2.16	1.08	.49	...	...	...	2.7	mg/l
tot V	3.6	2.5	3.4	2.1	1.3	...	...	...	2.7	mg/l
tot alk	4350	3300	4350	2600	2150	2450	4200	2050	3100	mg/l CaCO3
dis alk	4050	3100	4350	2450	2050	2350	4100	1850	3000	mg/l CaCO3
Cl	39	39	70	74	63	...	71	66	71	mg/l
SO4	176	166	173.6	185	151.6	...	197	170.6	192.6	mg/l as S
dis SiO2	6.62	4.85	6.11	4.66	4.71	...	8.91	5.64	5.55	mg/l as Si
B	.35	.32	.35	.32	.25	...	.45	.35	.3	mg/l
NO2	.03	.03	.22	.2	.23	...	.3	.23	...	mg/l as N
NO3	3	3.3	3.2	3.2	3	...	8.5	3.5	2.8	mg/l as N
NH3	.3	.1	1.2	.4	<.1	...	<.1	<.1	.2	mg/l as N
F	2.2	2.1	2.1	1.32	.96	...	1.75	1.5	2.3	mg/l
PO4	1.8	1.3	5	1.91	.56	...	3.1	1.18	.2	mg/l as P
EC	5900	4060	7350	4550	3180	4500	7500	4060	5300	mhos/cm
SS	151	151	175	190	187	204	159	215	139	mg/l

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LEACHATE TO KINGHORN LOCH for 27/2/81 to 2/5/81

date	27/2/81	9/3/81	14/3/81	21/3/81	29/3/81	30/3/81	9/4/81	20/4/81	2/5/81	
time	1135	1235	1105	1405	1810	1235	2000	2025	1725	
flow	1.3	3.4	6.5	4.8	5.3	4.5	3.2	2.2	3.1	l/s
temp	3.5	7	8.5	7	10.5	9.5	10.5	11	9	C
pH	12	12.2	12	10.8	11.4	11.5	11.5	11.9	11.8	
tot Ca	6.7	2.7	.8	.3	.2	...	.8	1.6	26.5	mg/l
dis Ca	...	...	...	.4	.3	...	.4	.4	15.2	mg/l
tot Mg	18.8	14.3	2.6	1.7	.3	...	1.2	.4	31.5	mg/l
dis Mg	...	...	...	<.1	.3	...	.3	<.1	.8	mg/l
Na	1524	2739	1902	1149	1432	...	1385	1762	1469	mg/l
K	22.7	31.8	22.4	17.5	19.8	...	19.7	18.7	15	mg/l
tot Al	114	188	165	97	132	...	102	104	101	mg/l
dis Al	...	...	...	95	133	...	95	102	107	mg/l
tot Fe	...	...	...	...	...	...	...	1.8	.2	mg/l
dis Fe	...	...	...	...	...	...	.1	.1	.2	mg/l
tot As	...	...	2.8	...	...	2.5	...	...	...	mg/l
tot V	...	...	4.6	...	...	3.8	...	...	...	mg/l
tot alk	3200	5150	3650	1800	2350	2700	2400	2545	3275	mg/l CaCO3
dis alk	3050	4950	3550	1800	2350	2550	2450	2825	2970	mg/l CaCO3
Cl	73	66	61	58	70	...	67	90	69	mg/l
SO4	188.3	166	69.7	146.2	115.3	...	70	103.3	140	mg/l as S
dis SiO2	5.55	4.29	7.41	1.11	2.7	...	6.34	7.97	8.81	mg/l as Si
B	.25	.35	.48	.38	.48	...	.48	.62	.45	mg/l
NO2	.28	.43	.28	.01	.26	...	.23	.23	1.76	mg/l as N
NO3	2.6	2.15	2	3	8.9	...	3.4	3	2.1	mg/l as N
NH3	.3	.49	.4	.1	.5	...	.3	<.1	.6	mg/l as N
F	2.5	2.3	2.1	2.4	2.8	...	2.6	2.2	1.4	mg/l
PO4	.24	3.5	1.5	.17	1.1	...	1.38	1.65	1.72	mg/l as P
EC	5200	7800	5550	3550	4625	5000	4650	5400	5200	mhos/cm
SS	175	192	50	135	92	89	97	112	279	mg/l

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LEACHATE TO KINGHORN LOCH for 17/5/81 to 9/7/81

date	17/5/81	23/5/81	1/6/81	8/6/81	13/6/81	21/6/81	28/6/81	1/7/81	9/7/81	
time	1950	1325	1745	1800	1155	2105	1825	1710	1030	
flow	1.8	1.1	1.1	3	3	1.8	.8	2.6	.8	l/s
temp	10	11.5	15	13	12	14	10	12	14	C
pH	12.1	12.1	12	11.6	12	12.4	12.3	12.4	12.3	
tot Ca	.8	7.9	7.1	9.5	6.2	14	6.4	8.7	1.2	mg/l
dis Ca	1.7	6.4	6.8	5.9	6.6	2.6	4.9	2.6	.9	mg/l
tot Mg	.9	4.6	3.2	5.8	4.5	17.3	9.3	5	23.3	mg/l
dis Mg	.3	3.9	.9	.9	.8	<.5	<.5	<.5	<.1	mg/l
Na	3170	1890	1912	1737	2080	2037	1999	2006	1787	mg/l
K	20.6	15.7	18.2	19.7	25.8	23.2	21.2	22	14.6	mg/l
tot Al	230	130	122	117	135	112	128	122	121	mg/l
dis Al	230	131	122	108	133	138	128	115	108	mg/l
tot Fe	1.1	.2	.2	.4	1.1	.8	.4	.5	.5	mg/l
dis Fe	.2	.1	.1	.1	.1	...	...	...	...	mg/l
tot As	3.3	...	...	...	3	...	...	...	...	mg/l
tot V	5	...	...	...	3.2	...	...	...	...	mg/l
tot alk	3000	3800	4400	1290	4200	5150	4900	4900	3800	mg/l CaCO3
dis alk	2950	3800	4400	...	4100	5000	4800	4850	3550	mg/l CaCO3
Cl	77	71	69	...	...	67	64	100	67	mg/l
SO4	133.3	68.3	150	118	101.6	134	150.3	168.6	152.3	mg/l as S
dis SiO2	8.07	8.16	8.44	5.17	8.49	9.89	9.33	9.51	12.36	mg/l as Si
B	.69	.62	.66	.5	1	1.05	.95	1	.6	mg/l
NO2	.61	.16	.14	.04	.05	1.25	.16	.03	.29	mg/l as N
NO3	1.7	1.7	1.8	1.5	7	1.2	1.3	1.4	.3	mg/l as N
NH3	.5	.8	1.1	<.1	<.1	.8	.9	1.3	1.5	mg/l as N
F	.76	.7	.72	.52	2.3	.75	.85	1.7	2	mg/l
PO4	7	1.7	2	.87	2.75	2	3	2.4	9.6	mg/l as P
EC	6000	5700	5850	5000	6500	7100	7200	7000	6400	mhos/cm
SS	231	15	21	56	38	147	81	56	290	mg/l

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LEACHATE TO KINGHORN LOCH for 20/7/81 to 9/9/81

date	20/7/81	21/7/81	25/7/81	3/8/81	9/8/81	18/8/81	24/8/81	2/9/81	9/9/81	
time	1725	1310	1405	0910	1220	1620	1035	1800	0920	
flow	.8	...	1	1.8	.87	.7	1.3	.7	.7	l/s
temp	12	...	12	14	12	14	12	12	12	C
pH	12.3	12.3	12.1	12.4	12.3	12.3	12.3	12.2	12.3	
tot Ca	3.2	...	3.2	4.3	7.9	14.9	8	9.6	34.7	mg/l
dis Ca	.8	...	1.8	<.1	.6	.4	.7	.1	1.1	mg/l
tot Mg	5.3	...	7.3	6.1	10.9	23.7	10.4	11	14.2	mg/l
dis Mg	<.1	...	8.9	<.1	6.8	.1	.6	.1	.1	mg/l
Na	1615	...	1381	2025	1810	2030	1740	1530	1800	mg/l
K	14	...	14.5	16.9	24	27	25	23	25	mg/l
tot Al	113	131	78	118	126	134	108	94	98	mg/l
dis Al	98	...	79	114	126	129	107	91	96	mg/l
tot Fe	.4	...	.1	.3	<.1	3.4	.2	.1	.3	mg/l
dis Fe	...	...	...	...	...	...	...	...	...	mg/l
tot As	...	...	...	3.1	...	...	3.3	...	...	mg/l
tot V	...	...	...	6.8	...	...	5.1	...	...	mg/l
tot alk	3400	3670	2700	4050	3960	4250	3500	3500	3850	mg/l CaCO3
dis alk	3250	3050	2670	4050	3960	3850	3485	3500	3600	mg/l CaCO3
Cl	63	...	73	64	64	63	21	71	70	mg/l
SO4	344.6	...	183.3	81.3	240	206.6	223.3	223.3	190	mg/l as S
dis SiO2	9.51	...	6.06	9.79	8.63	3.26	9.23	1.77	6.01	mg/l as Si
B	.5	...	.5	.4	.5	1.45	.6	.5	.55	mg/l
NO2	.18	...	.6	.27	1.66	.99	1.22	1.15	.86	mg/l as N
NO3	1.7	...	2.7	1.9	1.7	1.2	6.3	1.4	1	mg/l as N
NH3	.8	...	.9	1.25	1.06	.7	.9	.6	.5	mg/l as N
F	3	...	4.8	5.7	1.45	.54	.58	.4	.38	mg/l
PO4	1.89	...	1.55	...	2.8	3.1	.11	1.9	...	mg/l as P
EC	5300	6400	5300	7600	5800	6100	6100	5600	5800	mhos/cm
SS	45	81	52	87	40	420	108	82	99	mg/l

LEACHATE TO KINGHORN LOCH for 15/9/81 to 1/11/81

date	15/9/81	16/9/81	24/9/81	28/9/81	5/10/81	12/10/81	20/10/81	30/10/81	1/11/81	
time	1025	1700	1400	1745	1450	0945	1500	1555	1015	
flow	.3	1	1.54	1.82	4	2.7	2.6	1.8	2.6	l/s
temp	12	12	11	13	12	6	8	9	9	C
pH	12.1	12.3	12.6	12.5	12.3	12.2	12.3	12.1	12.1	
tot Ca	...	13.3	5.5	5	28.7	2	1.7	3.5	2.1	mg/l
dis Ca	...	6	2.4	2.4	3.9	1.6	1.7	2	2.6	mg/l
tot Mg	...	.6	.3	8	5.3	.4	.4	.4	.7	mg/l
dis Mg	...	1.3	.2	1.1	1.4	.2	.3	.3	.4	mg/l
Na	...	2030	3710	3594	3594	2432	2186	2380	2522	mg/l
K	...	29	48	32.4	32.4	28.4	27.8	30.4	30.4	mg/l
tot Al	98	107	280	284	258	181	139	146	161	mg/l
dis Al	...	107	282	286	258	176	130	152	153	mg/l
tot Fe	...	.42	.95	.37	.85	.5	.2	.3	2.5	mg/l
dis Fe	...	...	...	.27	.19	...	...	...	...	mg/l
tot As	3.8	...	...	...	...	...	...	3.4	...	mg/l
tot V	5.2	...	...	...	...	...	...	4.1	...	mg/l
tot alk	4500	4100	7250	8000	8850	5400	4650	5050	5060	mg/l CaCO3
dis alk	4250	4100	7300	8000	8650	5400	4650	5050	5050	mg/l CaCO3
Cl	...	71	83	90	82	69	72	71	64	mg/l
SO4	...	190	265.3	297	258.3	190	177	189	189	mg/l as S
dis SiO2	...	4.29	4.66	5.13	5.13	5.59	9.7	10.07	9.33	mg/l as Si
B	...	.05	.05	1.2	.85	.8	.55	.6	.6	mg/l
NO2	...	.85	.31	.28	.25	.23	.32	.25	.22	mg/l as N
NO3	...	.9	1.4	1.45	1.7	1.3	1.4	1.3	1.3	mg/l as N
NH3	...	.97	1.63	1.6	1.05	1	.26	.39	.35	mg/l as N
F	...	.46	.19	.2	3.7	4.3	2.3	2.5	2	mg/l
PO4	...	2.1	6.6	.76	5.8	2.9	1.85	4.6	4.4	mg/l as P
EC	6200	6900	10200	11800	11100	10500	8000	8400	8800	mhos/cm
SS	94	96	81	50	58	53	29	65	89	mg/l

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LEACHATE TO KINGHORN LOCH for 8/11/81 to 29/12/81

date	8/11/81	9/11/81	16/11/81	22/11/81	1/12/81	12/12/81	15/12/81	21/12/81	29/12/81	
time	1730	1405	1000	2000	0715	1055	2055	1000	1138	
flow	4.6	3.1	4.6	2.8	2.9	3.6	3.4	3	3	l/s
temp	9	...	5	10	5	3	2	4	3.5	C
pH	12	12.1	12.1	12.4	12.4	12.1	12.2	11.5	11.7	
tot Ca	2.5	...	10.9	.4	.5	2.7	2.7	2.9	1.3	mg/l
dis Ca	3.4	...	6.7	.4	<.5	3.3	2	1.9	1.3	mg/l
tot Mg	.4	...	4.1	1.7	2.2	.7	11.6	8.8	4.6	mg/l
dis Mg	.3	...	<.1	.7	<.5	11.7	<.5	<.5	<.5	mg/l
Na	2432	...	2028	2272	2007	1463	1557	1751	2343	mg/l
K	30.6	...	26.4	20.3	19	19.3	17.8	20.2	21	mg/l
tot Al	143	146	134	143	126	103	115	...	220	mg/l
dis Al	142	...	134	143	128	94	112	119	200	mg/l
tot Fe	.3	...	<.05	.2	.2	.15	.18	...	.16	mg/l
dis Fe	...	...	...	.2	.2	.14	.05	.06	.11	mg/l
tot As	...	4.9	...	...	...	...	...	5.6	...	mg/l
tot V	...	7.2	...	...	...	...	...	10	...	mg/l
tot alk	4750	5860	5300	4700	3770	3100	3190	3350	4800	mg/l CaCO3
dis alk	4750	4535	5300	4700	3600	3100	3135	3250	4800	mg/l CaCO3
Cl	67	...	69	70	66	84	65	64	51	mg/l
SO4	195	...	164	185.3	133.6	158.6	153.5	153.5	138	mg/l as S
dis SiO2	10.45	...	9.7	15.3	12.36	11.89	13.25	13.01	10.26	mg/l as Si
B	.6	...	.55	.5	.4	.4	.4	.4	.3	mg/l
NO2	.24	...	.23	.25	.2	.21	.22	1.62	.17	mg/l as N
NO3	2	...	1.6	1.9	1.2	2.1	2.2	2.3	2	mg/l as N
NH3	1	...	1.5	.7	.18	.68	.8	.6	.5	mg/l as N
F	2	...	1.8	1.6	2.2	2.4	2.4	2.7	2.4	mg/l
PO4	4.2	...	3.6	4.4	3.1	1.9	3	3.3	4.2	mg/l as P
EC	8100	9000	6800	6650	5200	5750	5200	5150	7800	mhos/cm
SS	33	33	19	29	44	79	102	80	49	mg/l

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LEACHATE TO KINGHORN LOCH for 1/1/82 to 1/3/82

date	1/1/82	10/1/82	19/1/82	26/1/82	1/2/82	9/2/82	10/2/82	21/2/82	1/3/82	
time	1020	1255	0910	1810	1315	1420	1325	1720	0820	
flow	3	6.1	4.6	8.5	3.6	3.4	...	3.1	2.9	l/s
temp	3.5	3	4.5	8	7	6	...	5	6	C
pH	11.7	12	12.2	12.2	11.8	11.1	12.3	12	11.8	
tot Ca	1.9	5.6	2.2	3.1	...	...	...	...	...	mg/l
dis Ca	.5	2.3	1.6	.8	1.9	2.4	...	2.7	.4	mg/l
tot Mg	4.8	16.7	8.6	18	...	...	...	...	...	mg/l
dis Mg	<.5	<.5	<.5	.6	1.2	.5	...	.11	<.1	mg/l
Na	2784	1237	1990	2238	1792	2158	...	1640	1408	mg/l
K	35.5	23.1	29.4	26.5	28.2	28.6	...	22.8	19.7	mg/l
tot Al	250	106	184	164	...	...	155	...	...	mg/l
dis Al	250	100	184	166	100	146	...	118	101	mg/l
tot Fe	.13	.09	.21	.12	...	...	...	...	...	mg/l
dis Fe	.13	.08	.11	...	<.05	<.05	...	.08	<.05	mg/l
tot As	...	...	3.3	...	...	...	3.7	...	...	mg/l
tot V	...	...	3.9	...	...	...	5.9	...	...	mg/l
tot alk	5400	4100	3750	4700	...	...	4220	...	...	mg/l CaCO3
dis alk	5400	4050	3750	4685	3400	4500	4050	3650	3500	mg/l CaCO3
Cl	68	67	159	61	66	61	...	66	67	mg/l
SO4	132	179.3	131	132.6	131	253.3	...	145	161.6	mg/l as S
dis SiO2	7.51	4.94	4.71	3.4	4.99	5.78	...	4.24	3.26	mg/l as Si
B	.475	.375	.35	.45	.475	.45	...	.4	.6	mg/l
NO2	.24	.29	.22	.27	.27	.26	...	.38	.27	mg/l as N
NO3	1.9	3.2	2.2	2.3	2	2	...	1.8	1.5	mg/l as N
NH3	.5	1	.7	.9	1.3	.4	...	.6	.4	mg/l as N
F	2.6	3.7	3.2	1.05	1.6	1.3	...	1.3	1.35	mg/l
PO4	5.5	1.7	2.5	3.5	2.3	3.05	...	2.35	1.68	mg/l as P
EC	9100	4700	7800	8800	6600	8200	7800	6600	4900	mhos/cm
SS	74	125	74	87	92	115	78	92	84	mg/l

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LEACHATE TO KINGHORN LOCH for 10/3/82 to 1/5/82

date	10/3/82	14/3/82	18/3/82	27/3/82	1/4/82	11/4/82	15/4/82	26/4/82	1/5/82	
time	1805	0935	1445	1830	0950	1715	2010	1940	1630	
flow	2	2.2	2.7	1.8	5.6	1.1	.8	.7	...	l/s
temp	5	6	...	9	7	6.5	...	10	...	C
pH	12.1	11.6	12.2	12.3	12.3	12.4	12.4	12.1	...	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	.3	.5	1.5	.7	.7	1	1.4	<.5	...	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	.3	.1	<.5	.4	.2	.14	.3	<.5	...	mg/l
Na	2000	1437	2011	1958	1942	2028	1938	1934	...	mg/l
K	20.98	18.9	12.2	27.4	26.1	28.9	28	23.6	...	mg/l
tot Al	...	...	158	...	...	...	...	...	...	mg/l
dis Al	169	104	165	157	156	151	145	112	...	mg/l
tot Fe	...	...	...	...	...	...	...	...	...	mg/l
dis Fe	<.05	<.05	<.05	<.05	<.05	.25	.28	.06	...	mg/l
tot As	...	...	4.4	...	...	4.6	...	...	...	mg/l
tot V	...	...	7.2	...	...	8	...	...	...	mg/l
tot alk	...	...	4950	...	...	...	...	...	...	mg/l
dis alk	4650	3450	4750	4500	4600	4550	4450	4100	...	mg/l CaCO3
Cl	62	71	67	62	61	64	65	72	...	mg/l CaCO3
SO4	132.6	132.6	132.6	130.6	149.3	160	160	126.6	...	mg/l
dis SiO2	3.91	3.35	6.99	9.33	8.86	8.86	8.86	8.39	...	mg/l as S
B	.45	.625	.45	.5	.5	.47	.47	.54	...	mg/l as Si
NO2	.25	.18	.27	.29	.24	.43	.28	.36	...	mg/l
NO3	1.3	1.1	1.1	1.1	1.2	1.1	1.1	1.5	...	mg/l as N
NH3	.4	.5	.8	.7	.83	.4	.4	1.1	...	mg/l as N
F	1.15	1.3	1.4	1.4	1.2	2.9	2.4	3.4	...	mg/l as N
PO4	2.8	2.3	5.7	3.15	3.8	3.2	2.5	4	...	mg/l
EC	7200	4950	7100	7500	7200	7900	7600	5800	...	mg/l as P
SS	38	168	94	83	74	86	82	60	...	mhos/cm
										mg/l

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LEACHATE TO KINGHORN LOCH for 11/5/82 to 8/7/82

date	11/5/82	18/5/82	26/5/82	1/6/82	7/6/82	16/6/82	23/6/82	1/7/82	8/7/82	
time	1045	1255	1020	0730	1600	1620	1600	0715	0815	
flow	1.4	.93	...	1.3	.8	4.4	.88	3.14	.84	l/s
temp	...	10	...	13	15	10	10.5	12	12	C
pH	12.2	12.2	12.3	12.3	12.2	12.1	12.1	12.2	12.3	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	8.6	8.6	9.5	8.7	6.2	7.7	1.1	1.7	2.2	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	.2	.5	1.1	1.1	.3	.9	.5	.1	.1	mg/l
Na	2121	1779	2241	2140	2057	2403	2337	2662	2633	mg/l
K	34.9	27.9	34	30.2	40.9	34.9	34.9	36	35.8	mg/l
tot Al	170	...	...	...	...	...	...	...	...	mg/l
dis Al	161	110	166	153	155	164	151	197	199	mg/l
tot Fe	...	...	...	...	...	...	...	...	...	mg/l
dis Fe	<.05	<.05	.29	.13	.14	.22	.14	.15	.14	mg/l
tot As	4.4	...	...	4.6	...	...	...	...	...	mg/l
tot V	7	...	...	7	...	...	...	...	...	mg/l
tot alk	4855	...	...	...	5500	5500	5000	...	...	mg/l CaCO3
dis alk	4855	3760	5185	4700	4950	5200	4800	5250	5600	mg/l CaCO3
Cl	60	72	60	65	62	66	62	60	69	mg/l
SO4	133	175	123	126	123	128.3	30.6	31.3	28.6	mg/l as S
dis SiO2	9.09	8.3	11.66	...	10.96	4.47	10.26	8.39	10.73	mg/l as Si
B	.675	.6	.8	.825	.825	.785	1.2	2.4	2.85	mg/l
NO2	.21	1.27	.2	.22	.26	.29	.19	.16	.19	mg/l as N
NO3	1.2	1.4	.8	1.2	.9	1.2	1.3	1	.9	mg/l as N
NH3	.9	.4	1.3	.6	1.3	.8	1	1.4	.8	mg/l as N
F	1.3	2.8	2.7	2.1	3.9	2.8	3.3	1.7	2.2	mg/l
PO4	3.7	2	4.5	2.9	3.3	4.4	2.05	4.7	2.6	mg/l as P
EC	9600	7400	10200	8600	9700	9700	8700	11000	10200	mhos/cm
SS	20	15	43	21	148	64	78	95	89	mg/l

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LEACHATE TO KINGHORN LOCH for 19/7/82 to 5/9/82

date	19/7/82	26/7/82	1/8/82	4/8/82	12/8/82	19/8/82	22/8/82	1/9/82	5/9/82	
time	2115	2150	1220	1135	1740	1740	1745	1200	1730	
flow	1.4	1.1	.88	.87	2.7	2.2	2	.93	.7	l/s
temp	15	14	14	...	13	11	12	12	10	C
pH	12	12.3	12.3	12.3	12.4	12.6	12.4	12.5	12.6	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	2	1.3	2	2.3	3.4	2.2	2.3	2.2	8.2	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	.3	<.1	<.1	1.9	1.7	.9	1.5	.4	.2	mg/l
Na	2406	2495	2349	2535	2366	2856	2790	2502	3299	mg/l
K	35.9	38.9	34.4	35.9	35.5	35.4	33.1	36.5	47.8	mg/l
tot Al	...	...	...	175	...	...	...	...	...	mg/l
dis Al	158	179	172	189	165	206	136	196	250	mg/l
tot Fe	...	...	...	...	...	...	...	...	...	mg/l
dis Fe	.19	.34	.16	.21	.26	.25	.15	.31	.17	mg/l
tot As	...	...	...	6.5	...	...	6	...	5.1	mg/l
tot V	...	...	...	9	...	...	6	...	8	mg/l
tot alk	...	...	...	...	...	...	...	...	...	mg/l CaCO3
dis alk	5300	5450	4800	5550	6350	6600	5250	6560	8595	mg/l CaCO3
Cl	74	72	68	68	113	65	68	68	70	mg/l
SO4	121	166.3	159.1	97.3	65	158.3	101	150.3	120.6	mg/l as S
dis SiO2	8.39	...	10.49	10.73	11.43	4.12	8.63	4.8	2.09	mg/l as Si
B	2	...	2.05	2.75	2.3	3	1.6	1.1	2.2	mg/l
NO2	.15	.18	.6	.23	.22	.17	.15	.19	.17	mg/l as N
NO3	1.3	1.2	1.15	1	.9	.8	1.2	.9	.5	mg/l as N
NH3	.6	.6	1.12	1.1	.8	.9	.5	1	.4	mg/l as N
F	1.8	4.4	2.25	2.4	2.1	2.5	1.8	2.3	3.5	mg/l
PO4	2	2.8	3	3	1.7	9.5	5.2	4.1	4.15	mg/l as P
EC	9900	12000	9800	11400	10200	10600	8600	9200	11100	mhos/cm
SS	40	50	51	78	55	164	38	98	34	mg/l

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LEACHATE TO KINGHORN LOCH for 12/9/82 to 8/11/82

date	12/9/82	19/9/82	23/9/82	26/9/82	1/10/82	10/10/82	26/10/82	1/11/82	8/11/82	
time	1140	1735	1140	1800	1800	1510	1630	0830	1220	
flow	...	1.36	...	7.52	1.26	3.9	2.2	2.8	6.9	l/s
temp	...	...	...	10	11.5	10	9.5	9	9	C
pH	...	12.7	12.6	12.7	12.6	12.7	12.4	12.4	12.8	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	...	2.8	...	10.5	3	1.5	.7	3.1	3.8	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	...	.2	...	.7	.3	1.8	<.5	<.5	<.5	mg/l
Na	...	2750	...	2472	2182	2976	1803	2596	2437	mg/l
K	...	43.8	...	35	37	37.2	24	35.9	32.2	mg/l
tot Al	...	...	165	...	...	...	...	...	...	mg/l
dis Al	...	196	...	143	111	264	135	211	216	mg/l
tot Fe	...	...	...	...	...	...	...	...	...	mg/l
dis Fe	...	.18	...	<.05	<.05	.72	.25	.1	.11	mg/l
tot As	...	...	4.4	...	...	...	4.6	...	...	mg/l
tot V	...	...	8.2	...	...	...	7.1	...	...	mg/l
tot alk	...	...	5500	...	...	...	...	...	...	mg/l CaCO3
dis alk	...	5950	5500	6150	5200	8300	3900	6050	5500	mg/l CaCO3
Cl	...	71	...	66	75	71	69	76	68	mg/l
SO4	...	125	...	122.6	127	121.3	117.6	117.6	128.3	mg/l as S
dis SiO2	...	4.99	...	5.69	7.13	3.87	7.41	4.89	5.27	mg/l as Si
B	...	2.1	...	1.4	1.425	2.725	1	1.325	1.2	mg/l
NO2	...	.18	...	.13	.12	.15	.24	.19	.17	mg/l as N
NO3	...	.9	...	.7	1.1	1.1	1.1	1.6	1.7	mg/l as N
NH3	...	1.1	...	.96	1	1.06	.5	1.1	.6	mg/l as N
F	...	2.8	...	3.1	9.2	11.5	2.8	13.5	11.5	mg/l
PO4	...	5.3	...	4.35	2.25	5.55	1.95	4.85	3.6	mg/l as P
EC	...	10950	10300	9500	8600	12600	7500	12600	10400	mhos/cm
SS	...	67	19	70	47	49	7	34	37	mg/l

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LEACHATE TO KINGHORN LOCH for 17/11/82 to 18/1/83

date	17/11/82	22/11/82	1/12/82	8/12/82	14/12/82	25/12/82	1/1/83	9/1/83	18/1/83	
time	1200	1800	0930	1810	1255	1350	1510	1615	1410	
flow	3.4	5.1	3.9	5.3	2.7	5	5	6.2	...	l/s
temp	5.5	5	5	5	5	6	5	5	...	C
pH	12.3	12.2	12.3	11.2	11.1	12.2	12.2	12.2	12.1	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	4.4	6.1	6.8	6.9	8	10	7	8.7	11	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	<.5	.3	<.5	<.5	.4	.6	.1	.1	1.2	mg/l
Na	1678	2362	1837	1864	1735	1600	1640	1710	840	mg/l
K	23.9	27.6	26.1	22.7	22.3	20.18	22.09	17.97	20.42	mg/l
tot Al	...	...	...	...	...	...	...	...	...	mg/l
dis Al	115	100	117	123.6	124	119.4	123.6	148.9	117	mg/l
tot Fe	...	...	...	...	...	...	...	...	...	mg/l
dis Fe	.13	.02	<.05	.07	.07	<.05	.07	.09	<.01	mg/l
tot As	...	...	...	...	4.1	...	...	...	...	mg/l
tot V	...	...	...	...	5	...	...	...	...	mg/l
tot alk	...	...	...	...	...	...	...	...	...	mg/l CaCO3
dis alk	4000	3750	4200	4850	4050	3000	3100	4450	3600	mg/l CaCO3
Cl	69	66	69	59	63	60	62	59	67	mg/l
SO4	125.6	123.3	124.6	125.6	128	129.5	129.6	127	163	mg/l as S
dis SiO2	2.05	4.94	7.09	6.11	6.85	4.1	7.37	3.21	8.63	mg/l as Si
B	.875	.95	.875	.775	.75	.5	.85	.8	.7	mg/l
NO2	.21	.22	.28	.23	.24	2.5	1.19	.18	.3	mg/l as N
NO3	1.6	1.5	2	2.6	1.3	2.5	1	2.3	2.45	mg/l as N
NH3	.2	.6	.6	.6	.2	.02	.02	.88	.7	mg/l as N
F	4.7	3.4	3.7	9	7.5	10	19.5	5.5	14.5	mg/l
PO4	2.5	3.5	2.2	2.45	2.3	1.85	2.2	1.85	1.75	mg/l as P
EC	7700	10000	7450	8300	7900	6600	7000	7600	6800	mhos/cm
SS	26	38	125	121	117	90	69	97	44	mg/l

LEACHATE TO KINGHORN LOCH for 24/1/83 to 7/3/83

date	24/1/83	1/2/83	9/2/83	15/2/83	20/2/83	26/2/83	28/2/83	1/3/83	7/3/83	
time	1455	1830	0735	1615	1140	1245	1300	1000	1600	
flow	4.4	5.1	3.2	3	1.5	1.3	3	2.4	1.5	l/s
temp	6.5	4	4	7	4	6	5	5	7.5	C
pH	12.2	12.3	12.2	12.3	12.2	12.4	12.1	12.6	10.4	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	6.1	6.2	9.1	10.9	9.5	9.9	...	4.8	2.5	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	2.6	4.4	.3	<.1	<.1	.2	...	<.1	1.2	mg/l
Na	1868	2140	1907	1710	1674	1698	...	2111	810	mg/l
K	20.91	27	27.7	20.75	20.6	21.36	...	26.2	15.38	mg/l
tot Al	...	...	...	...	...	...	2.7	...	...	mg/l
dis Al	132.3	164.2	124.9	109.1	116.2	108.7	...	151	14.4	mg/l
tot Fe	...	...	...	...	...	...	...	...	...	mg/l
dis Fe	<.01	.03	.5	<.01	<.01	.11	...	.18	<.01	mg/l
tot As	...	2.8	...	...	...	...	2.9	...	...	mg/l
tot V	...	1.8	...	...	...	...	3.6	...	...	mg/l
tot alk	...	...	...	...	...	...	3155	...	...	mg/l CaCO3
dis alk	3900	4650	5150	3850	3600	4450	3150	5350	1400	mg/l CaCO3
Cl	64	60	60	59	63	33	...	50	66	mg/l
SO4	163	163	200	148	148	185.3	...	155.6	241.6	mg/l as S
dis SiO2	8.16	3.03	9.33	9.09	8.63	9.09	...	5.59	.46	mg/l as Si
B	.85	.9	.9	.75	.7	.8	...	.9	.55	mg/l
NO2	.31	.28	.26	.23	.22	.42	...	.22	.26	mg/l as N
NO3	1.7	1.7	1.5	1.4	1.3	3.6	...	1.2	1.6	mg/l as N
NH3	1	.51	.5	1.1	.7	.4	...	.8	.26	mg/l as N
F	4.5	3.5	3.9	3.9	3.9	4.3	...	3.8	.39	mg/l
PO4	3.1	5	2.85	3.2	2.45	3	...	3.7	.4	mg/l as P
EC	8400	9000	8500	7700	7600	7600	5000	10000	2870	mhos/cm
SS	78	84	95	96	94	27	85	82	256	mg/l

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LEACHATE TO KINGHORN LOCH for 16/3/83 to 12/5/83

date	16/3/83	27/3/83	1/4/83	14/4/83	18/4/83	22/4/83	26/4/83	1/5/83	12/5/83	
time	0920	2000	1034	1800	1235	0710	1020	1645	1740	
flow	2	3.1	3	...	3.9	1.4	2.9	3.2	2.9	l/s
temp	7	5.5	6.5	9	6	10	7.5	9	11	C
pH	12.3	12.1	12.1	11.9	11.9	11.9	12	12.1	11.8	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	9.1	10.9	...	7	7.8	8.4	8.6	4.6	2	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	.2	<.1	...	4.4	7.3	2.2	5	6.9	<.1	mg/l
Na	2090	1590	...	1489	1642	1613	1810	2184	1480	mg/l
K	27	21.47	...	17.19	17.46	19.84	18.77	27	14.4	mg/l
tot Al	...	...	...	...	...	...	...	...	...	mg/l
dis Al	160.5	118	...	92	99	99	115	148	105	mg/l
tot Fe	...	...	...	...	...	...	...	...	...	mg/l
dis Fe	.08	<.01	...	.13	.13	.17	.2	.21	<.1	mg/l
tot As	...	...	...	3.6	...	...	...	...	3.4	mg/l
tot V	...	...	...	5.2	...	...	...	...	5.1	mg/l
tot alk	...	...	...	...	...	...	...	...	...	mg/l CaCO3
dis alk	4850	3650	3150	3300	3450	3450	3950	4600	3350	mg/l CaCO3
Cl	61	69	70	73	74	72	73	79	66	mg/l
SO4	186.6	238.3	241.6	151.6	241.6	206.6	153.3	165	110.3	mg/l as S
dis SiO2	5.31	6.25	6.43	6.81	7.09	6.9	7.04	6.53	5.78	mg/l as Si
B	.9	.8	.75	.8	.85	.8	.95	1.02	1	mg/l
NO2	.19	.37	.16	.15	.15	.17	.14	.15	1.65	mg/l as N
NO3	.9	1.4	1.2	1	1	1	1	.9	1.8	mg/l as N
NH3	.68	.4	.6	.84	1.06	.7	.79	.52	.21	mg/l as N
F	4.1	...	...	4.8	4.8	4.8	4.5	4.2	3.2	mg/l
PO4	4.6	2.8	1.7	3.25	3.1	2.5	2.8	3.85	1.4	mg/l as P
EC	9950	7800	6000	6700	7200	5800	6300	8400	6600	mhos/cm
SS	54	76	69	115	21	18	17	16	40	mg/l

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LEACHATE TO KINGHORN LOCH for 15/5/83 to 24/5/83

date	15/5/83	24/5/83	
time	1255	1100	
flow	2.3	1.1	l/s
temp	11	11	C
pH	11.9	11.9	
tot Ca	...	...	mg/l
dis Ca	1.6	12.3	mg/l
tot Mg	...	...	mg/l
dis Mg	<.1	.8	mg/l
Na	1674	1628	mg/l
K	18.01	16.84	mg/l
tot Al	...	...	mg/l
dis Al	120	98	mg/l
tot Fe	...	...	mg/l
dis Fe	<.1	.04	mg/l
tot As	...	...	mg/l
tot V	...	...	mg/l
tot alk	...	...	mg/l CaCO3
dis alk	3700	3350	mg/l CaCO3
Cl	70	67	mg/l
SO4	119	114	mg/l as S
dis SiO2	6.11	5.59	mg/l as Si
B	.85	.95	mg/l
NO2	.14	1.06	mg/l as N
NO3	1.5	1.1	mg/l as N
NH3	.38	.3	mg/l as N
F	2.5	3.3	mg/l
PO4	1.1	1.75	mg/l as P
EC	7200	6400	mhos/cm
SS	20	71	mg/l

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LEACHATE TO KINGHORN LOCH
statistical appraisal - for 4/1/81 to 24/5/83

	samples	maximum	minimum	mean	std.dev.	n20	n10	n5	
flow	120	8.5	.3	2.71866	1.62479	34	137	549	l/s
temp	115	15	2	8.50435	3.39278	15	61	245	C
pH	126	12.8	10.4	12.0913	.389871	58	234	1460	
tot Ca	53	34.7	.2	7.23396	7.48049	103	411	1643	mg/l
dis Ca	106	15.2	<.1	4.03066	3.4962	72	289	1156	mg/l
tot Mg	53	31.5	.3	8.2	7.17018	73	294	1175	mg/l
dis Mg	106	11.7	<.1	.987736	1.91565	361	1445	5780	mg/l
Na	117	3710	810	2006.55	524.292	7	26	105	mg/l
K	117	48	12.2	25.6284	7.48871	8	33	131	mg/l
tot Al	62	284	2.7	137.769	51.2048	13	53	212	mg/l
dis Al	112	286	14.4	139.748	46.9767	11	43	174	mg/l
tot Fe	43	3.4	<.05	.509418	.652588	158	630	2522	mg/l
dis Fe	83	.72	<.01	.126867	.115107	79	316	1265	mg/l
tot As	32	6.5	.49	3.56469	1.35602	14	56	222	mg/l
tot V	32	10	1.3	5.26875	2.20987	17	68	270	mg/l
tot alk	66	8850	1290	4125	1355.34	10	41	166	mg/l CaCO3
dis alk	125	8650	1400	4295.36	1293.73	9	35	139	mg/l CaCO3
Cl	116	159	21	67.8362	13.4797	4	15	61	mg/l
SO4	118	344.6	28.6	153.5	49.8975	10	41	162	mg/l as S
dis SiO2	116	15.3	.46	7.06699	2.8049	15	61	242	mg/l as Si
B	117	3	.05	.823162	.580615	48	191	765	mg/l
NO2	117	2.5	.01	.366153	.407779	119	476	1906	mg/l as N
NO3	118	8.9	.3	1.83898	1.31542	49	197	786	mg/l as N
NH3	118	1.63	.02	.680932	.376575	29	117	470	mg/l as N
F	116	19.5	.19	3.15965	2.96049	84	337	1349	mg/l
PO4	116	9.6	.11	2.95104	1.6362	30	118	472	mg/l as P
EC	126	12600	2870	7461.47	2087.9	8	30	120	mhos/cm
SS	126	420	7	87.1587	63.1575	50	202	807	mg/l

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LEACHATE TO KINGHORN LOCH
statistical appraisal — for 4/1/81 to 24/5/83

	samples	maximum	minimum	mean	std.dev.	n20	n10	n5	
tot Ca	53	114.8	.959999	17.2978	21.7938	152	610	2439	mg/s
dis Ca	103	78.96	.07	11.1914	13.8194	146	586	2343	mg/s
tot Mg	53	153	.462	21.9699	28.5727	162	650	2599	mg/s
dis Mg	103	42.12	<.230001	2.57973	5.98959	518	2071	8284	mg/s
Na	114	19023	1071	5424.35	3609.09	43	170	680	mg/s
K	114	263.2	11.2	68.3018	45.9734	44	174	696	mg/s
tot Al	59	1394	8.1	371.674	282.046	55	221	885	mg/s
dis Al	109	1490.4	21.6	377.438	276.627	52	206	825	mg/s
tot Fe	43	6.5	.07	1.09028	1.25512	127	509	2036	mg/s
dis Fe	80	2.808	<.015001	.319845	.384415	139	555	2220	mg/s
tot As	29	18.2	1.14	8.30879	4.67339	30	122	486	mg/s
tot V	29	30	1.56	11.8597	6.99404	33	134	534	mg/s
tot alk	63	39950	1350	10884.9	7797.37	49	197	789	mg/s CaCO3
dis alk	119	46248	1275	11571.7	8221.5	48	194	776	mg/s CaCO3
Cl	113	731.4	27.3	184.738	119.744	40	161	646	mg/s
SO4	115	1127.1	24.024	407.043	252.428	37	148	591	mg/s as S
dis SiO2	113	49.616	.69	18.1495	11.5452	39	155	622	mg/s as Si
B	114	10.6275	.05	2.11314	1.86762	75	300	1200	mg/s
NO2	114	12.5	.03	.944815	1.45785	229	915	3659	mg/s as N
NO3	115	47.17	.24	5.51877	6.18886	121	483	1932	mg/s as N
NH3	115	7.65	.1	1.7798	1.62541	80	320	1282	mg/s as N
F	113	97.5	.266	9.55822	14.124	210	839	3355	mg/s
PO4	113	32.712	.143	8.09658	6.70919	66	264	1055	mg/s as P
SS	120	864.9	13.95	234.623	197.703	68	273	1091	mg/s

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TABLE A.2. Chemical analysis of the north inlet to Kinghorn Loch (at Craigencalt Farm) for the period 4-1-1981 to 24-5-1983; including statistical appraisal.

N. INLET TO KINGHORN LOCH for 4/1/81 to 27/2/81

date	4/1/81	9/1/81	20/1/81	25/1/81	29/1/81	9/2/81	15/2/81	23/2/81	27/2/81	
time	1620	0955	1300	1205	0910	1105	1655	1620	1035	
flow	40	44	36	40	36	33	33	26	26	l/s
temp	7	4	4	5	5.5	5.5	5	3.5	3.5	C
pH	8.4	8.3	8.1	8.1	8.2	8.3	8.1	8	8	
tot Ca	55.8	57.1	...	...	...	56.3	51.9	41.9	43	mg/l
dis Ca	...	...	...	...	...	...	...	...	...	mg/l
tot Mg	24.1	22.4	...	...	...	22.8	23.3	25.6	25.5	mg/l
dis Mg	...	...	...	...	...	...	...	...	...	mg/l
Na	22.9	23.1	...	...	...	25.4	22.4	28.2	28.3	mg/l
K	.7	.7	...	...	...	.4	.6	.8	.5	mg/l
tot Al	<.1	<.1	<.1	<.1	...	...	...	...	...	mg/l
dis Al	...	<.1	<.1	...	...	...	...	...	...	mg/l
tot Fe	...	.5	.1	<.1	<.1	...	...	...	...	mg/l
dis Fe	...	...	...	...	...	...	...	...	...	mg/l
tot As	<.005	.01	<.005	<.005	<.005	...	...	...	...	mg/l
tot V	<.1	<.1	<.1	<.1	<.1	...	...	...	...	mg/l
tot alk	120	115	125	125	125	140	145	140	140	mg/l CaCO3
dis alk	130	120	125	125	125	135	145	140	135	mg/l CaCO3
Cl	25	25	27	28	24	40	39	40	40	mg/l
SO4	48.3	42.6	35	44.3	35.6	29.3	46.6	33.6	25.3	mg/l as S
dis SiO2	5.22	5.03	4.85	5.13	4.8	4.75	5.17	4.52	4.19	mg/l as Si
B	.07	.07	.07	.09	.05	.05	.08	.05	.05	mg/l
NO2	.01	.01	.01	.01	.01	.05	.04	.08	.05	mg/l as N
NO3	9	8.6	9.6	9.6	9	2.9	3.4	3	3.9	mg/l as N
NH3	.1	.2	<.1	.1	.2	.7	.1	.1	<.1	mg/l as N
F	.1	.2	.2	.2	.2	.1	.1	.1	.1	mg/l
PO4	.02	.01	.04	.05	.01	.03	.01	.02	.02	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
EC	410	392	445	440	414	445	425	395	380	mhos/cm
SS	3	1	1	3	1	2	3	3	3	mg/l

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N.INLET TO KINGHORN LOCH for 9/3/81 to 12/5/81

date	9/3/81	14/3/81	21/3/81	29/3/81	9/4/81	20/4/81	26/4/81	2/5/81	12/5/81	
time	1300	1110	1420	1815	2020	1950	2015	1700	1815	
flow	33	53	49	44	33	26	23	23	20	l/s
temp	5.5	7	6	7	8	...	7.5	8	10.5	C
pH	8.2	8	8.2	7.9	7.8	8.2	8.1	8.1	8	
tot Ca	42.5	34.9	37.8	39.8	45	41.9	40.3	49.6	55.9	mg/l
dis Ca	...	...	38	41	41.4	40.1	41	44.4	40.7	mg/l
tot Mg	27.3	28	26.3	27.5	24.9	26.2	24.5	22.6	21.8	mg/l
dis Mg	...	...	20.3	21.1	23.1	20.8	20.8	19.8	19.4	mg/l
Na	27.4	23.1	21.7	24.9	21.6	25.3	27.6	21.1	20	mg/l
K	.5	2.2	1.1	.5	.5	.3	.1	.4	.3	mg/l
tot Al	...	...	...	...	...	...	...	...	...	mg/l
dis Al	...	...	...	...	...	...	...	...	...	mg/l
tot Fe	...	...	...	...	...	.2	.3	.2	<.1	mg/l
dis Fe	...	...	...	...	...	...	...	...	...	mg/l
tot As	...	...	...	...	...	...	...	...	...	mg/l
tot V	...	...	...	...	...	...	...	...	...	mg/l
tot alk	135	125	130	125	125	140	135	130	120	mg/l CaCO3
dis alk	135	125	130	125	125	...	...	...	...	mg/l CaCO3
Cl	24	22	21	23	24	23	22	22	25	mg/l
SO4	26	20.3	17.6	17.3	10.6	51.3	52	51.3	26	mg/l as S
dis SiO2	4.15	10.73	4.1	5.17	4.52	5.13	5.27	3.68	3.26	mg/l as Si
B	.08	.08	.09	.05	.1	.1	.14	.1	.05	mg/l
NO2	.02	.04	<.01	<.01	.01	.02	.03	.02	.04	mg/l as N
NO3	8.6	8.1	8.5	8.4	8.7	8.1	7.9	7.6	7.4	mg/l as N
NH3	.12	.3	<.1	.1	<.1	<.1	.13	.29	<.1	mg/l as N
F	.1	.2	.18	.2	.16	.18	.16	.13	.075	mg/l
PO4	.01	.22	.68	.01	.02	.01	.02	.03	<.01	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
EC	397	350	405	420	415	410	500	415	383	mhos/cm
SS	2	100	43	3	1	4	7	12	1	mg/l

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N. INLET TO KINGHORN LOCH for 17/5/81 to 20/7/81

date	17/5/81	23/5/81	1/6/81	8/6/81	13/6/81	21/6/81	28/6/81	1/7/81	20/7/81	
time	1910	1310	1730	1750	1125	2055	1830	1655	1715	
flow	20	20	3	2.5	2	1.3	1.3	1.3	1.1	l/s
temp	11	13	12	11	11	11	11	...	11	C
pH	8.2	8.3	8.1	8.1	8.1	8	8.1	8.3	8.6	
tot Ca	56.4	51.4	58.9	62.2	60.5	52.1	49.6	50.3	43.8	mg/l
dis Ca	45.4	43.3	47.5	62	60	52.7	48.2	48.6	41.1	mg/l
tot Mg	21.9	20.7	22.3	24.4	21.2	21.5	20	22.7	28.8	mg/l
dis Mg	19.3	20	21.2	24	21	21.9	22.3	22.6	24.9	mg/l
Na	19.2	19.6	18.8	23.8	23.9	19.6	18.6	17.5	13.9	mg/l
K	<.1	<.1	.4	.7	.2	.8	1.5	.6	.8	mg/l
tot Al	<.1	.5	.1	.2	<.1	.4	.2	.3	.1	mg/l
dis Al	<.1	.2	<.1	.1	<.1	...	...	...	...	mg/l
tot Fe	<.1	.1	.1	<.1	<.1	.3	.4	.1	.5	mg/l
dis Fe	...	...	...	...	...	...	...	...	...	mg/l
tot As	...	...	...	...	...	...	...	...	...	mg/l
tot V	...	...	...	...	...	...	...	...	...	mg/l
tot alk	115	130	140	155	140	150	140	145	165	mg/l CaCO3
dis alk	...	...	...	...	...	150	140	145	...	mg/l CaCO3
Cl	25	25	24	...	...	23	23	29	22	mg/l
SO4	27.3	30	27.3	22.3	24.3	68.3	30	36	18.6	mg/l as S
dis SiO2	3.07	2.93	4.57	4.66	1.25	4.61	4.94	4.66	4.8	mg/l as Si
B	.05	.1	<.05	.1	.1	.05	.05	.05	.1	mg/l
NO2	.03	.02	.02	.03	.01	.05	.01	<.01	<.01	mg/l as N
NO3	7.2	6.5	8	2.5	1.3	6.2	6.9	7.3	6.9	mg/l as N
NH3	<.1	<.1	<.1	.1	1.2	.2	.1	.1	.1	mg/l as N
F	.026	.05	.046	<.02	.09	.2	.19	.17	.027	mg/l
PO4	<.01	.02	.05	<.01	.01	.02	.01	.12	.06	mg/l as P
BOD	...	...	...	...	1.1	...	...	...	...	mg/l as O
EC	392	345	392	420	393	392	390	408	430	mhos/cm
SS	8	<1	1	<1	9	1	10	4	1	mg/l

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N.INLET TO KINGHORN LOCH for 25/7/81 to 24/9/81

date	25/7/81	3/8/81	9/8/81	18/8/81	24/8/81	2/9/81	9/9/81	16/9/81	24/9/81	
time	1350	0920	1245	1810	1015	1820	0940	1730	1425	
flow	1.3	1.2	1	.8	1.2	.87	1	.76	1	l/s
temp	12	17	12	11	11	11	12	11	11	C
pH	8.5	8.4	8.6	8.4	8.2	8.3	8.4	8.2	8.2	
tot Ca	44.4	45.7	69.3	68.3	74.2	69.1	57.8	63.4	68.5	mg/l
dis Ca	39.1	39.5	65.1	68	74.2	69	57.8	69.5	70.2	mg/l
tot Mg	23.8	23.8	28.1	27.9	28.2	27	25.6	24.8	26.2	mg/l
dis Mg	24.9	24.9	26.3	27.7	28	27	25.6	24.2	26.4	mg/l
Na	21.3	19.7	15	13	22	17	14	21	19	mg/l
K	.7	1	.5	.5	.8	.8	.8	.9	1	mg/l
tot Al	.5	.5	.1	.2	.2	.3	.5	.5	.3	mg/l
dis Al	.4	.3	.2	.2	.2	.2	.2	.5	.3	mg/l
tot Fe	<.1	.1	<.1	<.1	<.1	.1	<.1	.06	.05	mg/l
dis Fe	...	...	...	...	...	...	...	...	...	mg/l
tot As	...	...	...	...	...	...	...	...	...	mg/l
tot V	...	...	...	...	...	...	...	...	...	mg/l
tot alk	205	160	160	145	150	145	140	135	140	mg/l CaCO3
dis alk	205	160	160	145	150	145	140	85	140	mg/l CaCO3
Cl	28	21	23	24	38	23	23	25	28	mg/l
SO4	24.6	18.3	27.3	28	27.6	26.6	23.6	24.3	25.6	mg/l as S
dis SiO2	8.16	4.38	4.75	5.22	4.99	4.01	5.03	4.75	4.57	mg/l as Si
B	.1	.1	.1	.05	.01	.05	.1	.15	.15	mg/l
NO2	.01	.01	.01	.01	.01	.01	.02	<.01	<.01	mg/l as N
NO3	6.6	6.8	6.4	6.3	6.2	5.6	5.3	5.8	5.5	mg/l as N
NH3	<.1	.02	.06	.1	<.1	<.1	.1	.05	.02	mg/l as N
F	.04	.06	.11	.064	.093	.061	.064	.056	.051	mg/l
PO4	.01	.05	.11	.04	.05	.02	...	.07	<.01	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
EC	445	455	380	458	406	420	390	363	405	mhos/cm
SS	2	<1	1	1	2	1	9	5	3	mg/l

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N.INLET TO KINGHORN LOCH for 28/9/81 to 22/11/81

date	28/9/81	5/10/81	12/10/81	20/10/81	30/10/81	1/11/81	8/11/81	16/11/81	22/11/81	
time	1800	1440	0915	1525	1545	1000	1710	1015	2015	
flow	2	12.2	14	7.4	7.4	9.2	12.2	9.2	18.3	l/s
temp	11	11	8	9	8	8	8	8	8	C
pH	8.2	8.2	8.1	8.3	8.1	8.1	8	8.2	8.1	
tot Ca	83.4	85.1	48.8	51.5	44.7	47	48	73.4	26.2	mg/l
dis Ca	76.6	84.1	44.8	44.2	40.7	41.7	41.3	64.1	23.3	mg/l
tot Mg	28	28	30.3	30.6	29	29.5	29.7	28.8	29.5	mg/l
dis Mg	28.1	27.9	24.6	24.6	23.8	24.1	24.1	28.1	28.6	mg/l
Na	25	22.6	21.7	21.4	19.9	19.6	20.2	23.1	20.9	mg/l
K	.6	.6	.6	.5	.5	.6	.4	.5	.4	mg/l
tot Al	.5	.4	.5	.8	.9	1.1	1.6	.8	.7	mg/l
dis Al	.3	.4	<.5	<.5	<.1	<.1	<.1	<.1	<.1	mg/l
tot Fe	.11	.04	.4	.3	.5	.2	<.1	.1	.3	mg/l
dis Fe	.03	.03	...	...	...	...	...	...	.1	mg/l
tot As	...	...	...	...	...	...	...	...	...	mg/l
tot V	...	...	...	...	...	...	...	...	...	mg/l
tot alk	150	120	145	120	130	130	140	145	130	mg/l CaCO3
dis alk	150	120	145	120	130	130	...	145	130	mg/l CaCO3
Cl	27	25	22	22	19	20	22	23	25	mg/l
SO4	29	25.3	28.6	27	27	27	20	22.6	23.6	mg/l as S
dis SiO2	4.99	5.22	5.36	5.64	6.2	4.99	5.36	4.89	7.37	mg/l as Si
B	.1	.05	.15	.1	.05	.1	.1	.1	.05	mg/l
NO2	<.01	.01	<.01	.01	.01	.01	.01	<.01	<.01	mg/l as N
NO3	5.8	7.2	7.5	6.8	5.8	6.4	6.6	6	7.3	mg/l as N
NH3	.07	.04	<.1	.03	.03	.07	.1	<.1	.3	mg/l as N
F	.067	.12	.1	.16	.4	.43	.35	.23	.3	mg/l
PO4	.04	<.01	.02	.02	<.01	<.01	.02	.01	.01	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
EC	380	355	447	391	347	376	428	385	394	mhos/cm
SS	2	5	4	<1	1	7	3	1	4	mg/l

N. INLET TO KINGHORN LOCH for 1/12/81 to 26/1/82

date	1/12/81	12/12/81	15/12/81	21/12/81	29/12/81	1/1/82	10/1/82	19/1/82	26/1/82	
time	0720	1105	2045	0940	1027	1015	1235	0840	1555	
flow	30.7	19.7	11.2	11.2	29	32.5	48.7	36.2	32.5	l/s
temp	7	1	5	4	7	3.5	3.5	4.5	3	C
pH	8.1	7.7	8.1	7.6	7.1	7.8	8	7.9	8	
tot Ca	27.4	58.3	38.3	44.7	27.4	30.9	41.6	44.1	43.6	mg/l
dis Ca	23.5	38	38.8	43.5	32.7	29.5	44.7	44.1	42.3	mg/l
tot Mg	30.3	33.3	21	20.8	14.1	11.3	19.2	18.6	38.5	mg/l
dis Mg	28.6	20.8	20.3	20.5	14.5	11.7	19.6	19.8	35.9	mg/l
Na	20.2	22.1	17.8	15.5	17.4	20.8	18.8	19.9	22.6	mg/l
K	.5	.3	.43	.47	2.4	.47	.62	.6	.6	mg/l
tot Al	.74	.56	.38	.38	.6	.4	.42	<.2	<.1	mg/l
dis Al	.74	.56	.38	.16	.2	.2	.21	<.2	<.1	mg/l
tot Fe	.4	.27	.05	<.05	.68	1.17	<.05	<.05	.07	mg/l
dis Fe	.1	<.05	.06	<.05	.61	.07	<.05	.07	...	mg/l
tot As	...	...	...	...	...	...	...	...	...	mg/l
tot V	...	...	...	...	...	...	...	...	...	mg/l
tot alk	120	85	130	100	60	75	100	105	120	mg/l CaCO3
dis alk	120	85	...	100	60	75	100	...	...	mg/l CaCO3
Cl	19	25	23	21	25	14	21	26	25	mg/l
SO4	41.6	25.6	28.3	26.5	21.9	13	21.6	20	21	mg/l as S
dis SiO2	7.83	6.15	5.92	5.73	4.75	4.15	4.66	4.75	4.57	mg/l as Si
B	<.05	<.05	<.05	<.05	<.05	.05	.05	.025	.025	mg/l
NO2	<.01	<.01	<.01	.02	.05	.02	<.01	<.01	.01	mg/l as N
NO3	7.1	7.5	7.8	7.8	5.6	4	8.7	8	8.6	mg/l as N
NH3	.02	.79	<.01	.4	.7	.1	<.1	.1	.7	mg/l as N
F	.1	.08	.16	.15	.16	.13	.14	.11	.066	mg/l
PO4	.01	.01	.01	.01	.01	<.01	.01	.01	.01	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
EC	320	383	355	358	289	210	390	440	470	mhos/cm
SS	6	7	4	1	11	<1	2	3	<1	mg/l

N. INLET TO KINGHORN LOCH for 1/2/82 to 1/4/82

date	1/2/82	9/2/82	21/2/82	1/3/82	10/3/82	14/3/82	18/3/82	27/3/82	1/4/82	
time	1300	1400	1735	0805	1820	0950	1510	1900	1020	
flow	30.7	25.7	13.3	11.2	10.2	9.2	7.6	8.3	6.6	l/s
temp	6	5	4.5	5.5	5	5	...	5	6	C
pH	8	8	8.1	8.1	8.2	8.1	8.2	8.1	8.2	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	35.1	40.6	42.6	39.9	17.4	19.7	49.8	37	37	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	36.2	36.3	34.6	27.6	36.1	36.6	24.9	36.8	36.1	mg/l
Na	20.4	21	22.5	22.9	21.1	21.6	19.5	28.5	24.5	mg/l
K	.6	.6	.7	.7	.45	.46	.6	.77	.68	mg/l
tot Al	...	...	...	...	...	...	<.1	...	...	mg/l
dis Al	<.1	<.1	<.1	<.1	<.1	<.1	.1	.1	.1	mg/l
tot Fe	...	...	...	...	...	...	...	...	...	mg/l
dis Fe	<.05	<.05	.06	<.05	<.05	<.05	.08	<.05	<.05	mg/l
tot As	...	...	...	...	...	...	<.1	...	...	mg/l
tot V	...	...	...	...	...	...	<.1	...	...	mg/l
tot alk	...	...	...	...	...	...	135	...	...	mg/l CaCO3
dis alk	120	125	140	130	135	135	135	110	130	mg/l CaCO3
Cl	23	24	27	29	26	24	29	28	36	mg/l
SO4	21	13.6	13	16.6	20.6	23	20	23	19.6	mg/l as S
dis SiO2	4.19	4.19	3.82	3.59	3.96	3.87	4.66	4.66	3.96	mg/l as Si
B	.05	.025	.05	.05	.125	.025	.05	.06	<.05	mg/l
NO2	<.01	.01	<.01	.02	.02	.01	.02	.01	.01	mg/l as N
NO3	6.6	8	8.6	8.3	8	7.7	8	7.8	8.2	mg/l as N
NH3	.2	.1	<.1	.1	.2	.1	.2	.2	.01	mg/l as N
F	.09	.086	.064	.082	.066	.065	.065	.082	.082	mg/l
PO4	.01	<.01	<.01	.01	.22	<.01	.07	.03	<.01	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
EC	410	455	455	400	425	435	400	405	420	mhos/cm
SS	4	2	3	2	1	1	1	2	2	mg/l

N.INLET TO KINGHORN LOCH for 11/4/82 to 7/6/82

date	11/4/82	15/4/82	26/4/82	1/5/82	11/5/82	18/5/82	26/5/82	1/6/82	7/6/82	
time	1745	1950	0715	1655	1100	1315	0950	0710	1630	
flow	5.2	6.6	2.8	...	5.2	5.2	17	12.2	12.2	l/s
temp	5.5	...	7.5	9	...	9.5	12	13.5	16.5	C
pH	8.1	8	8.1	8.3	8.1	8.2	8.3	8.2	8.1	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	25.6	26	37.2	37.1	37.2	35.9	35.1	36	32.9	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	40.9	41	17.6	17.5	18.9	18.3	18.2	17.9	17.3	mg/l
Na	22.2	27.4	20.3	20.5	21.8	27.1	17.9	21.6	21.2	mg/l
K	.67	.74	.56	.51	.6	.6	.5	.44	1.9	mg/l
tot Al	...	...	...	...	<.1	...	...	...	...	mg/l
dis Al	<.1	<.1	.2	<.1	.4	<.1	<.1	.1	<.1	mg/l
tot Fe	...	...	...	...	...	...	...	...	...	mg/l
dis Fe	.12	.18	.08	.21	<.05	<.05	.17	.22	.07	mg/l
tot As	...	...	...	...	<.0005	...	...	...	...	mg/l
tot V	...	...	...	...	<.1	...	...	...	...	mg/l
tot alk	...	...	...	...	150	...	...	...	...	mg/l
dis alk	135	140	145	150	150	140	140	135	130	mg/l CaCO3
Cl	25	26	27	25	24	28	25	24	...	mg/l CaCO3
SO4	19	19	19	21	19	24	5.3	5.3	28	mg/l
dis SiO2	3.91	4.47	4.75	1.11	2.84	3.4	2.42	2.33	5	mg/l as S
B	.05	.07	<.05	<.05	.075	.05	.05	.05	3.4	mg/l as Si
NO2	.01	.02	.02	.01	.03	.01	.03	.05	.05	mg/l
NO3	7.8	8	8	7.4	6.8	6.5	5.8	5.4	.05	mg/l as N
NH3	<.1	<.1	.1	<.1	<.1	<.1	<.1	.1	4.8	mg/l as N
F	.19	.2	.15	.17	.11	.2	.17	.17	.1	mg/l as N
PO4	<.01	<.01	.02	.01	.03	<.01	.01	.01	.23	mg/l
BOD	...	...	...	...	...	...	...	...	.01	mg/l as P
EC	425	450	355	475	455	450	450	430	430	mg/l as O
SS	3	2	4	2	2	4	1	2	4	mhos/cm
										mg/l

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N.INLET TO KINGHORN LOCH for 16/6/82 to 19/8/82

date	16/6/82	23/6/82	1/7/82	8/7/82	19/7/82	26/7/82	1/8/82	12/8/82	19/8/82	
time	1600	1625	0735	0835	2100	2205	1240	1750	1800	
flow	5.2	5	14.5	19.7	1.6	2.6	2.6	2.6	2.3	l/s
temp	10	10.5	10	10	10.5	12	12	11	10	C
pH	8.1	8.1	8.1	8	8	7.9	8.6	8.3	7.9	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	39.5	43.9	26.5	44.5	45.3	44.5	46.2	45.5	39.7	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	17.4	19.3	19.1	19	18.5	18.4	18.5	19	16.6	mg/l
Na	19.6	26.3	17.5	17.8	8.5	25.4	14.8	12.6	8.3	mg/l
K	.8	.7	.6	.6	.8	.8	.7	.9	.9	mg/l
tot Al	...	...	...	...	...	...	...	...	...	mg/l
dis Al	<.1	<.1	.2	.2	.2	.1	.1	<.1	<.1	mg/l
tot Fe	...	...	...	...	...	...	...	...	...	mg/l
dis Fe	.15	.12	.04	.04	.12	.13	.09	.07	.14	mg/l
tot As	...	...	...	...	...	...	...	...	...	mg/l
tot V	...	...	...	...	...	...	...	...	...	mg/l
tot alk	150	150	...	...	...	...	...	...	...	mg/l
dis alk	150	...	150	145	155	240	160	150	175	mg/l CaCO3
Cl	29	28	25	27	26	28	23	25	21	mg/l CaCO3
SO4	17.6	5	4.6	5	18.6	20.2	14.4	17.3	31.6	mg/l
dis SiO2	5.59	5.36	4.8	4.1	4.66	...	4.66	4.24	4.05	mg/l as S
B	.025	.05	.05	.05	.05	...	.05	.05	.05	mg/l as Si
NO2	.05	.07	.05	.1	.04	.03	.02	.02	.01	mg/l
NO3	8.1	8.75	8	7.8	7.3	8	7	7.6	5.6	mg/l as N
NH3	.2	.07	.1	<.1	<.1	.1	.02	<.1	<.1	mg/l as N
F	.18	.18	.1	.34	.17	.32	.23	.34	.26	mg/l
PO4	.03	.16	.06	.01	.01	<.01	.01	.06	.06	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
EC	460	430	475	370	405	480	445	430	350	mhos/cm
SS	2	2	2	1	6	1	2	2	4	mg/l

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N. INLET TO KINGHORN LOCH for 22/8/82 to 26/10/82

date	22/8/82	1/9/82	5/9/82	12/9/82	19/9/82	26/9/82	1/10/82	10/10/82	26/10/82	
time	1730	1215	1720	1150	1720	1820	0620	1520	1650	
flow	1.5	1.9	2.6	5.2	3.71	5.9	5.2	32.5	22.6	l/s
temp	11.5	10.5	16	11.5	10	10	10	10	8.5	C
pH	8.1	8.2	8.6	8.3	8.3	8.3	8.5	7.9	8.2	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	39.9	46.2	42.6	54.6	54.3	46.5	47	40	52.5	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	19.5	18.1	15.8	19.2	19.3	20.2	20	17.9	19.1	mg/l
Na	21	20.7	17.3	22	23	21.9	23.5	16.9	24.9	mg/l
K	.8	.8	1.6	.7	.7	.7	.7	2.3	.6	mg/l
tot Al	...	...	...	...	...	...	...	...	...	mg/l
dis Al	.3	.3	<.1	<.1	<.1	.8	.6	.6	.2	mg/l
tot Fe	...	...	...	...	...	...	...	...	...	mg/l
dis Fe	.15	<.01	.02	.05	.13	.3	.17	.23	.14	mg/l
tot As	...	...	...	...	...	...	...	...	...	mg/l
tot V	...	...	...	...	...	...	...	...	...	mg/l
tot alk	...	...	...	...	...	...	...	...	...	mg/l CaCO3
dis alk	160	150	135	155	145	150	160	130	140	mg/l CaCO3
Cl	28	25	26	24	28	25	25	26	23	mg/l
SO4	19.6	25	23.3	25	23.3	20.6	21.6	20.3	21.6	mg/l as S
dis SiO2	4.52	4.1	3.63	3.87	4.19	5.36	5.31	5.31	5.64	mg/l as Si
B	.05	.05	.05	.05	.05	.1	.075	.025	.025	mg/l
NO2	.01	.01	.02	.01	.04	.02	.01	.02	.01	mg/l as N
NO3	6.8	7.1	6.5	7	7.8	7.7	8.2	7.75	7.9	mg/l as N
NH3	<.1	<.1	<.1	<.1	<.1	.03	.04	.14	.1	mg/l as N
F	.18	.23	.24	.18	.18	.15	.24	.14	.07	mg/l
PO4	.1	.06	.08	<.01	.14	.05	.02	.2	.01	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
EC	430	360	420	520	430	395	420	380	410	mhos/cm
SS	<1	1	14	3	5	5	4	123	3	mg/l

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N. INLET TO KINGHORN LOCH for 1/11/82 to 1/1/83

date	1/11/82	8/11/82	17/11/82	22/11/82	1/12/82	8/12/82	14/12/82	25/12/82	1/1/83	
time	0850	1245	1225	1740	1005	1745	1300	1330	1540	
flow	17	40.2	22.6	22.6	29	34	29	10	22.6	l/s
temp	9	9	7.75	7	7	7	5	6	5	C
pH	7.6	8	8.2	7.9	8	7.8	8.1	8	8.2	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	46.1	46.1	40.2	42.5	50.7	43.1	41.7	43.3	41.7	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	20.2	19	18.6	15	18.5	18.3	18.4	18.1	18.1	mg/l
Na	22.5	25.6	21.5	26	23.8	22.8	24	19.6	20.4	mg/l
K	.6	.6	.5	1.5	.5	.7	.7	.6	.61	mg/l
tot Al	...	...	...	...	...	...	...	...	...	mg/l
dis Al	.3	.3	.3	.7	.3	<.1	<.1	<.1	<.1	mg/l
tot Fe	...	...	...	...	...	...	...	...	...	mg/l
dis Fe	.3	<.05	.07	.09	<.05	.12	.1	<.05	.07	mg/l
tot As	...	...	...	...	...	...	...	...	...	mg/l
tot V	...	...	...	...	...	...	...	...	...	mg/l
tot alk	...	...	...	...	...	...	...	...	...	mg/l CaCO3
dis alk	160	160	155	120	145	130	135	110	145	mg/l CaCO3
Cl	23	23	24	25	24	24	25	24	24	mg/l
SO4	22.6	20.3	16.6	16.6	21.6	18.8	22	22.1	22	mg/l as S
dis SiO2	5.45	5.41	4.94	3.96	5.03	4.8	4.8	4.38	4.38	mg/l as Si
B	.025	.05	.025	.025	.05	.05	.075	<.05	.05	mg/l
NO2	<.01	.02	.02	.02	.01	<.01	.01	.01	.01	mg/l as N
NO3	8.2	8.4	8.4	7.4	8.6	8.1	8.2	1.8	1.95	mg/l as N
NH3	<.1	.1	<.1	.8	<.1	<.1	<.1	.04	.05	mg/l as N
F	.09	.09	.07	.15	.07	.06	.08	.07	.12	mg/l
PO4	.01	.02	.01	.09	.02	.01	<.01	<.01	.02	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
EC	435	400	410	385	425	435	485	390	405	mhos/cm
SS	6	9	4	2	4	8	5	5	19	mg/l

N. INLET TO KINGHORN LOCH for 12/1/83 to 1/3/83

date	12/1/83	18/1/83	24/1/83	1/2/83	9/2/83	15/2/83	20/2/83	26/2/83	1/3/83	
time	1300	1410	1520	1845	0720	1630	1155	1230	1025	
flow	...	27.3	18	17	13.3	12.1	9.2	3.9	5.2	l/s
temp	9	5	6	4	5	5	5	5	5	C
pH	8	8	8.1	8	8.1	7.7	7.9	7.8	...	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	37.6	41.6	39.8	40.9	41.3	40.5	35	40	...	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	16.3	19	19.3	20.7	18.9	18.8	18.1	19	...	mg/l
Na	18.7	19.5	20.1	22.8	20.1	21	20.6	22	...	mg/l
K	.9	.52	.42	.69	.46	.51	.45	.73	...	mg/l
tot Al	...	...	...	...	...	...	...	...	...	mg/l
dis Al	<.1	<.1	<.1	<.1	.17	<.1	.17	.17	.1	mg/l
tot Fe	...	...	...	...	...	...	...	...	...	mg/l
dis Fe	.07	<.01	<.01	<.01	<.01	<.01	.04	<.01	...	mg/l
tot As	...	...	...	...	...	...	...	...	...	mg/l
tot V	...	...	...	...	...	...	...	...	...	mg/l
tot alk	...	...	...	...	...	...	...	...	...	mg/l
dis alk	135	140	130	150	140	145	135	155	...	mg/l CaCO3
Cl	23.4	26	16	26	24	23	28	25	...	mg/l CaCO3
SO4	20.3	16.3	19.3	16.3	22.3	19.3	7.3	14.6	...	mg/l
dis SiO2	4.19	4.43	4.47	4.57	5.13	4.89	4.66	4.47	...	mg/l as S
B	<.05	.05	.05	.05	.05	.05	.05	.1	...	mg/l as Si
NO2	.01	<.01	<.01	<.01	<.01	.01	<.01	.01	...	mg/l
NO3	8.7	9.1	8	8.6	8.8	9.5	9.2	8.7	...	mg/l as N
NH3	<.1	<.01	<.01	.74	.1	.05	<.1	.1	...	mg/l as N
F	.2	.07	.11	.11	.105	.105	.15	.009	...	mg/l as N
PO4	.02	.01	<.01	.04	.01	.01	<.01	.02	...	mg/l
BOD	...	...	...	...	...	...	...	...	...	mg/l as P
EC	355	435	445	437	435	435	455	435	...	mg/l as O
SS	22	6	7	7	2	3	1	3	...	mhos/cm
										mg/l

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N.INLET TO KINGHORN LOCH for 7/3/83 to 1/5/83

date	7/3/83	16/3/83	27/3/83	1/4/83	14/4/83	18/4/83	22/4/83	26/4/83	1/5/83	
time	1620	0900	2020	1001	1815	1515	0720	1100	1620	
flow	8.3	5.9	19.7	9.2	11.2	9.2	9.2	8.3	8.3	l/s
temp	6	6	5	6	6.5	7	6.5	6.5	8	C
pH	8	8	8	8.1	...	8.2	8.1	8.1	7.8	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	43.3	43.9	37.1	...	39.3	37.3	39.5	30.1	40.8	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	19.5	19.3	18	...	22.6	24.9	27.5	22.2	25	mg/l
Na	21	22.8	18.6	...	17.4	16.6	13.7	18.1	17.3	mg/l
K	.52	.57	.49	...	.64	.37	.7	.28	.5	mg/l
tot Al	...	...	...	...	...	...	...	...	...	mg/l
dis Al	<.1	.17	.35	...	.23	.23	.11	.11	<.1	mg/l
tot Fe	...	...	...	...	...	...	...	...	...	mg/l
dis Fe	.1	.1	<.01	...	.08	.02	.05	.08	.11	mg/l
tot As	...	...	...	...	...	...	...	...	...	mg/l
tot V	...	...	...	...	...	...	...	...	...	mg/l
tot alk	...	...	...	...	...	...	...	...	...	mg/l
dis alk	140	140	120	130	135	120	120	120	135	mg/l CaCO3
Cl	28	23	26	28	43	29	29	28	28	mg/l CaCO3
SO4	22.6	22.3	23.3	21.3	21.6	24	24	24.6	19	mg/l
dis SiO2	4.43	4.05	4.43	4.33	4.33	4.38	3.4	4.24	4.19	mg/l as S
B	.05	.05	.05	.05	.05	.05	.05	.05	.05	mg/l as Si
NO2	.01	.01	.01	.01	.01	.005	.01	.025	.001	mg/l
NO3	9	7.8	8.7	9	8.8	8.8	8.3	8.7	8.6	mg/l as N
NH3	.07	.02	<.1	<.1	.94	.06	<.1	.16	.007	mg/l as N
F	.092	.02	...	...	.078	.078	.078	.08	.145	mg/l as N
PO4	.02	.01	.02	.01	<.01	.02	.02	.01	.02	mg/l
BOD	...	...	...	.9	...	...	...	...	...	mg/l as P
EC	415	420	435	415	448	430	435	385	420	mg/l as O
SS	4	1	3	4	4	2	4	4	1	mhos/cm
										mg/l

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N.INLET TO KINGHORN LOCH for 12/5/83 to 24/5/83

date	12/5/83	15/5/83	24/5/83	
time	1755	1315	1115	
flow	8.3	8.8	15.7	l/s
temp	7	7	9	C
pH	8	7.5	8	
tot Ca	...	...	...	mg/l
dis Ca	37.1	37.5	35.3	mg/l
tot Mg	...	...	...	mg/l
dis Mg	17.5	16.6	19.4	mg/l
Na	20.3	20.8	19.8	mg/l
K	.68	1.03	.47	mg/l
tot Al	...	...	...	mg/l
dis Al	<.1	.2	<.1	mg/l
tot Fe	...	...	...	mg/l
dis Fe	<.1	<.1	<.01	mg/l
tot As	...	...	...	mg/l
tot V	...	...	...	mg/l
tot alk	...	...	...	mg/l CaCO3
dis alk	125	130	140	mg/l CaCO3
Cl	29	25	27	mg/l
SO4	15.6	19	13	mg/l as S
dis SiO2	4.29	3.35	3.59	mg/l as Si
B	.05	.15	.05	mg/l
NO2	.02	.105	.01	mg/l as N
NO3	7.9	7	8.3	mg/l as N
NH3	.02	1.9	<.1	mg/l as N
F	.105	.125	.105	mg/l
PO4	.02	.33	.02	mg/l as P
BOD	...	...	...	mg/l as O
EC	410	415	415	mhos/cm
SS	4	22	35	mg/l

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N.INLET TO KINGHORN LOCH
statistical appraisal - for 4/1/81 to 24/5/83

	samples	maximum	minimum	mean	std.dev.	n20	n10	n5	
flow	118	53	.76	15.2944	13.1419	71	284	1135	l/s
temp	115	17	1	8.00652	3.06302	14	56	225	C
pH	118	8.6	7.1	8.09832	.216274	18	72	449	
tot Ca	51	85.1	26.2	51.0588	13.3633	7	26	105	mg/l
dis Ca	107	84.1	17.4	43.3674	11.2408	6	26	103	mg/l
tot Mg	51	38.5	11.3	25.1412	4.61175	3	13	52	mg/l
dis Mg	107	41	11.7	22.4075	5.87314	7	26	106	mg/l
Na	115	28.5	8.3	20.7896	3.67736	3	12	48	mg/l
K	115	2.4	<.1	.676609	.376607	30	119	476	mg/l
tot Al	42	1.6	<.1	.386428	.330821	70	282	1126	mg/l
dis Al	99	.8	<.1	.173838	.166724	88	353	1413	mg/l
tot Fe	44	1.17	<.05	.190341	.223563	132	530	2120	mg/l
dis Fe	75	.61	<.01	.0836	.090905	114	454	1817	mg/l
tot As	7	<.1	<.0005	.010035	.017888	305	1221	4882	mg/l
tot V	7	<.1	<.1	.05	0	0	0	0	mg/l
tot alk	59	205	60	132.542	21.7028	3	10	41	mg/l CaCO3
dis alk	103	240	60	136.748	21.8024	2	10	39	mg/l CaCO3
Cl	117	43	14	25.5761	4.40489	3	11	46	mg/l
SO4	119	68.3	4.6	23.3849	9.90582	17	69	276	mg/l as S
dis SiO2	118	10.73	1.11	4.60542	1.13041	6	23	93	mg/l as Si
B	118	.15	.01	.060466	.030661	25	99	395	mg/l
NO2	119	.105	.001	.018453	.0184	95	382	1528	mg/l as N
NO3	119	9.6	1.3	7.25421	1.6683	5	20	81	mg/l as N
NH3	119	1.9	.007	.147243	.258176	295	1181	4724	mg/l as N
F	117	.43	.009	.136008	.079957	33	133	531	mg/l
PO4	118	.68	<.01	.037627	.077502	407	1630	6519	mg/l as P
BOD	2	1.1	.9	1	...	...	...	...	mg/l as O
EC	119	520	210	411.958	40.8353	1	4	15	mhos/cm
SS	119	123	<1	6.20588	15.1215	570	2281	9123	mg/l

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N. INLET TO KINGHORN LOCH

statistical appraisal - for 4/1/81 to 24/5/83

	samples	maximum	minimum	mean	std.dev.	n20	n10	n5	
tot Ca	51	2512.4	48.18	805.56	692.306	71	284	1135	mg/s
dis Ca	105	2176.89	45.21	538.919	484.682	78	311	1243	mg/s
tot Mg	51	1484	18.848	440.631	401.042	80	318	1273	mg/s
dis Mg	105	1166.75	18.392	289.069	262.284	79	316	1265	mg/s
Na	113	1224.3	10.4	323.694	296.693	81	323	1291	mg/s
K	113	116.6	.4	10.4145	15.7453	220	878	3512	mg/s
tot Al	42	22.718	.1	4.72957	6.27601	169	676	2706	mg/s
dis Al	97	22.718	<.371001	2.35925	3.93016	267	1066	4264	mg/s
tot Fe	44	38.025	.045599	3.51028	7.10631	394	1574	6298	mg/s
dis Fe	73	17.69	<.019	1.19391	2.33998	369	1476	5903	mg/s
tot As	7	<.760001	<.002601	.171614	.167352	91	365	1461	mg/s
tot V	7	<4.4	<.520001	1.49143	.812556	29	114	456	mg/s
tot alk	59	6625	102.6	2199.64	1897.02	71	286	1143	mg/s CaCO3
dis alk	101	6625	64.6	1986.27	1709.23	71	284	1138	mg/s CaCO3
Cl	115	1320	19	394.977	337.517	70	281	1122	mg/s
SO4	117	1932	18.468	378.573	425.94	122	486	1945	mg/s as S
dis SiO2	116	568.69	2.5	75.228	78.646	105	420	1679	mg/s as Si
B	116	4.41	.012	.90653	.95031	106	422	1689	mg/s
NO2	117	2.12	.0083	.288501	.420299	204	815	3261	mg/s as N
NO3	117	429.3	2.6	115.621	109.842	87	347	1387	mg/s as N
NH3	117	23.1	.02	2.5412	4.7137	330	1322	5287	mg/s as N
F	115	10.6	.0297	2.06462	2.22312	111	445	1782	mg/s
PO4	116	33.32	<.01	.742008	3.30813	1909	7636	30543	mg/s as P
BOD	2	8.28	2.2	5.24	...	...	...	...	mg/s as O
SS	117	5300	<1.5	156.116	636.317	1596	6382	25528	mg/s

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TABLE A.3. Chemical analysis of the north inlet to Kinghorn Loch (at Craigencalt Farm) for the period 30-5-1983 to 27-9-1984; including statistical appraisal.

N.INLET TO KINGHORN LOCH for 30/5/83 to 10/7/83

date	30/5/83	31/5/83	5/6/83	14/6/83	22/6/83	28/6/83	1/7/83	8/7/83	10/7/83	
time	1815	1225	1645	1810	1915	1600	0830	0725	0830	
flow	12.9	13.3	25	15.7	11.8	11.2	11.2	8.3	7.4	l/s
temp	8	...	8	8	8.5	11	9	10	10	C
pH	8.1	7.9	8	8	7.9	8.1	7.9	7.9	7.2	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	43.2	...	34.5	38.2	36.2	33.8	39	40.8	39.2	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	20	...	19	32.5	18.2	19.6	21.1	18.3	18.5	mg/l
Na	25	...	17.1	18.9	17.5	19.9	20.2	22.2	21.5	mg/l
K	1.3	...	.12	.56	.33	.41	.39	.4	.4	mg/l
tot Al	...	.5	...	...	...	...	...	...	...	mg/l
dis Al	<.1	...	.2	<.1	.1	<.1	.1	<.1	.1	mg/l
dis Fe	<.01	...	<.1	...	<.01	.04	.06	.05	.06	mg/l
tot As	...	<.005	...	...	...	...	...	...	...	mg/l
tot V	...	<.1	...	...	...	...	...	...	...	mg/l
tot alk	...	130	...	...	...	...	...	...	...	mg/l
dis alk	135	130	125	140	140	140	125	130	125	mg/l CaCO3
Cl	26	...	25	28	35	25	27	26	24	mg/l CaCO3
SO4	18.3	...	15.3	9.6	16.3	16.3	22.3	22.6	24	mg/l
dis SiO2	4.15	...	3.12	4.01	3.84	3.84	3.87	3.84	5.59	mg/l as S
B	.05	...	.05	.05	.05	.05	.05	.05	.15	mg/l as Si
NO2	.01	...	.03	.02	.01	.01	<.01	.01	<.01	mg/l
NO3	8.6	8.2	6.8	8	7.5	4	8.7	<.1	8.5	mg/l as N
NH3	<.1	...	.1	.1	<.1	<.1	<.1	<.1	.1	mg/l as N
F	.13	...	.105	.14	.12	.13	.145	.115	.12	mg/l as N
PO4	.04	...	<.01	.05	<.01	.02	.01	.02	<.01	mg/l
BOD	.9	...	...	...	...	...	...	...	...	mg/l as P
COD	...	...	...	...	...	...	...	...	...	mg/l as O
EC	405	390	430	425	410	430	430	440	455	mg/l as O
SS	5	2	3	4	4	1	2	5	2	mhos/cm
										mg/l

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N. INLET TO KINGHORN LOCH for 18/7/83 to 20/9/83

date	18/7/83	26/7/83	1/8/83	6/8/83	8/8/83	20/8/83	1/9/83	12/9/83	20/9/83	
time	0840	0810	1555	1740	1015	2045	1120	0930	0720	
flow	5.9	5.2	6.3	6.5	...	4.5	3.6	3.9	5.2	l/s
temp	...	11	11	12	...	12.5	11	10	10	C
pH	8	8.1	8	8.2	7.9	7.9	7.9	8.1	8.2	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	43.5	52.8	52.9	23.4	...	23.9	23.4	42.9	43.6	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	19.2	19.2	19.4	18.6	...	18.3	18.2	18.2	18.6	mg/l
Na	24.4	23	22	11.9	...	18.4	16.2	21.6	21.6	mg/l
K	.4	.6	.6	.5	...	.6	.6	.5	.5	mg/l
tot Al	...	...	...	...	<.1	...	...	...	...	mg/l
dis Al	.1	...	...	.2	<.1	.1	.1	.1	.1	mg/l
dis Fe	<.05	<.05	<.05	<.05	...	<.05	<.05	<.05	<.05	mg/l
tot As	...	...	...	...	<.005	...	...	...	...	mg/l
tot V	...	...	...	...	<.1	...	...	...	...	mg/l
tot alk	...	...	...	...	125	...	...	...	...	mg/l CaCO3
dis alk	125	100	120	155	125	135	155	130	135	mg/l CaCO3
Cl	27	26	26	27	...	27	25	24	25	mg/l
SO4	23.6	23.6	25	23.6	...	28	15.6	15.6	14.3	mg/l as S
dis SiO2	5.36	6.29	5.13	4.66	...	5.13	5.08	4.94	5.55	mg/l as Si
B	.1	.1	.1	.05	...	...	...	.05	.1	mg/l
NO2	<.01	.01	.01	.01	...	.03	.05	<.01	.03	mg/l as N
NO3	8	7.4	7.6	7.7	...	7.4	7	7.1	6.7	mg/l as N
NH3	.1	<.1	<.1	<.1	...	.2	.3	.1	<.1	mg/l as N
F	.11	.44	.32	.25	...	.16	.2	.15	.1	mg/l
PO4	<.01	.02	.03	.01	...	.04	.05	.04	.05	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
COD	...	...	...	...	...	...	...	...	...	mg/l as O
EC	450	455	435	350	385	450	410	430	470	mhos/cm
SS	7	2	2	<1	2	<1	6	<1	3	mg/l

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N. INLET TO KINGHORN LOCH for 24/9/83 to 9/11/83

date	24/9/83	28/9/83	1/10/83	9/10/83	20/10/83	25/10/83	2/11/83	7/11/83	9/11/83	
time	0725	1110	0945	1655	0900	1800	0835	1725	1020	
flow	5.2	...	3.3	5.9	15	12.2	9.2	10.2	8.3	l/s
temp	10.5	...	10.5	...	9	9.5	9	10	...	C
pH	8.2	8.2	8.2	8.2	8.2	8.1	8.1	8	8.2	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	50.5	35	41.2	41.2	38.9	43.4	42	42	31.3	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	19	15.4	18.2	18.1	18.6	18.4	18.4	18.3	17.8	mg/l
Na	21	19.8	20.5	19.8	21	19.7	18.3	23.1	22	mg/l
K	.7	.5	.7	.6	.56	.62	.52	.59	.62	mg/l
tot Al	...	.3	...	...	...	...	...	...	1.1	mg/l
dis Al	.1	.2	.1	.1	<.1	.1	.1	.4	.3	mg/l
dis Fe	.03	<.01	.25	.06	<.01	<.01	<.01	<.01	.05	mg/l
tot As	...	<.005	...	...	...	...	...	...	.008	mg/l
tot V	...	<.1	...	...	...	...	...	...	<.1	mg/l
tot alk	...	140	...	...	...	...	...	...	150	mg/l CaCO3
dis alk	145	130	150	145	135	150	150	155	150	mg/l CaCO3
Cl	23	27	25	25	26	27	27	25	25	mg/l
SO4	14.3	...	20	20	19.6	18.3	18.3	21	19.6	mg/l as S
dis SiO2	5.36	3.63	5.31	5.41	4.85	4.85	4.66	5.13	4.94	mg/l as Si
B	.08	.23	.1	.05	.05	.05	.05	.05	.05	mg/l
NO2	.01	.03	.01	.01	.01	<.01	<.01	.02	<.01	mg/l as N
NO3	6.6	7	6.7	6.9	9	8.8	8.5	8.6	8.4	mg/l as N
NH3	.1	.02	.2	.1	.01	.01	.02	.01	<.1	mg/l as N
F	.13	...	.2	.27	.19	.13	.15	.23	.18	mg/l
PO4	.03	.04	<.01	.06	<.01	<.01	<.01	.05	<.01	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
COD	...	...	...	...	...	...	...	...	...	mg/l as O
EC	455	470	440	435	385	445	420	440	445	mhos/cm
SS	1	6	13	5	6	5	<1	1	<1	mg/l

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N.INLET TO KINGHORN LOCH for 19/11/83 to 17/1/84

date	19/11/83	23/11/83	27/11/83	1/12/83	12/12/83	24/12/83	28/12/83	1/1/84	17/1/84	
time	0830	0720	1515	1655	1425	00	1445	1340	1130	
flow	5.2	5.2	5.2	4.9	5.2	...	29	...	1.65	l/s
temp	4	4	5.5	5.5	.5	...	8	7.5	6.5	C
pH	8.1	8.1	8.2	8.2	8.1	7.6	7.6	7.6	8.1	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	41.3	43.8	41.2	42.1	42.8	35	39	43.9	39.7	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	18.5	18.7	18.7	19.2	18.5	16.6	19.3	18.1	16.4	mg/l
Na	21.9	21.9	23.5	24.3	22.9	17.7	20.3	20.8	17.5	mg/l
K	.55	.53	.69	.68	.57	.41	1.04	.59	.52	mg/l
tot Al	...	...	...	...	...	...	...	...	...	mg/l
dis Al	.1	.1	.1	<.1	.1	.1	.1	.1	.2	mg/l
dis Fe	<.01	<.01	<.01	<.01	.05	.07	.04	.09	.07	mg/l
tot As	...	...	...	...	...	...	...	...	...	mg/l
tot V	...	...	...	...	...	...	...	...	...	mg/l
tot alk	...	...	...	...	...	...	...	...	...	mg/l
dis alk	135	145	140	145	135	125	125	110	105	mg/l CaCO3
Cl	28	28	...	...	...	27	29	27	29	mg/l CaCO3
SO4	14	14.6	13.3	13.3	13.3	19.6	20.6	17.3	18.3	mg/l
dis SiO2	4.66	4.66	4.66	4.66	4.94	3.96	3.91	4.01	4.05	mg/l as S
B	.05	.05	.1	.1	.05	.025	.15	.05	.025	mg/l as Si
NO2	<.01	<.01	...	...	...	<.01	<.01	<.01	<.01	mg/l
NO3	8.2	8.2	8.4	8.4	6.5	9.1	9.3	9.4	11.4	mg/l as N
NH3	.01	<.01	<.1	<.1	<.01	<.1	<.1	<.1	<.1	mg/l as N
F	...	...	...	...	...	...	...	.21	.17	mg/l
PO4	<.01	.01	...	...	...	<.01	.02	.03	.03	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
COD	...	...	...	...	...	...	...	...	...	mg/l as O
EC	430	425	400	400	435	325	340	395	415	mhos/cm
SS	5	4	3	2	3	9	8	15	2	mg/l

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N.INLET TO KINGHORN LOCH for 29/1/84 to 21/3/84

date	29/1/84	1/2/84	6/2/84	20/2/84	22/2/84	29/2/84	6/3/84	11/3/84	21/3/84	
time	1535	1015	1315	0735	1530	1050	1015	1740	0940	
flow	40.2	38	66	18.8	19.7	19.7	12.2	9.2	29	l/s
temp	6	6	5	6.5	6.5	6	8.5	7	7.5	C
pH	7.9	8	7.8	7.8	7.6	7.8	8	7.9	8	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	39.6	42.4	37.9	50.3	49.3	58.5	45.2	49.7	47.9	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	17.4	18.1	15.46	19.24	17.59	18.78	18.96	19.27	16.13	mg/l
Na	18.2	19	15.8	16.7	12.7	20.3	20	23.4	64.5	mg/l
K	.78	.66	1.76	.5	.73	.45	.34	.47	2.32	mg/l
tot Al	...	...	...	...	...	<.1	...	...	...	mg/l
dis Al	<.12	<.1	<.1	.2	.1	<.1	.8	.4	.6	mg/l
dis Fe	.16	.02	.19	.09	.02	.07	.01	.02	.03	mg/l
tot As	...	...	...	...	...	...	...	...	...	mg/l
tot V	...	...	...	...	...	...	...	...	...	mg/l
tot alk	...	...	...	...	...	...	...	...	...	mg/l CaCO3
dis alk	110	120	100	120	140	125	115	120	140	mg/l CaCO3
Cl	31	29	29	28	29	28	31	33	34	mg/l
SO4	18.3	19.6	13.3	17	17.6	17	16	17	17	mg/l as S
dis SiO2	4.15	4.1	3.91	4.33	4.47	3.77	5.97	5.78	5.64	mg/l as Si
B	.05	.025	<.025	.05	.075	.075	.05	.05	<.05	mg/l
NO2	.01	.005	.01	.005	.01	<.01	.08	.01	.01	mg/l as N
NO3	10.5	12.3	11.4	12.8	12.7	12.4	12.5	12	12.5	mg/l as N
NH3	.09	.05	.1	.1	<.1	<.1	.03	.05	.05	mg/l as N
F	.18	.18	.23	.16	.21	.21	.13	.15	.13	mg/l
PO4	.02	.03	.04	.02	.01	.02	.02	.01	.02	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
COD	...	...	...	...	...	...	...	...	...	mg/l as O
EC	405	435	305	430	445	430	425	425	425	mhos/cm
SS	16	2	14	2	2	2	4	2	8	mg/l

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N.INLET TO KINGHORN LOCH for 28/3/84 to 27/9/84

date	28/3/84	16/4/84	20/4/84	20/4/84	27/9/84	
time	1055	1930	0...	0...	0905	
flow	31.4	12.2	...	...	4	l/s
temp	6.5	7	...	...	11	C
pH	8	8.1	8	...	8.1	
tot Ca	...	...	...	<.1	...	mg/l
dis Ca	43.5	44.4	43.7	...	51.4	mg/l
tot Mg	...	...	...	.2	...	mg/l
dis Mg	18.45	18.6	18.3	...	20	mg/l
Na	17.9	20.4	19.1	899	23.5	mg/l
K	.55	.46	.46	1.49	.9	mg/l
tot Al	...	...	...	356	...	mg/l
dis Al	.4	<.1	<.1	...	...	mg/l
dis Fe	.18	...	...	...	<.05	mg/l
tot As	...	...	<.005	.6	...	mg/l
tot V	...	...	<.1	1.3	...	mg/l
tot alk	...	...	...	...	...	mg/l CaCO3
dis alk	135	110	120	...	145	mg/l CaCO3
Cl	33	29	31	13	31	mg/l
SO4	13.6	16.6	...	...	20	mg/l as S
dis SiO2	4.66	4.85	4.99	.79	4.57	mg/l as Si
B	.05	.05	...	...	.05	mg/l
NO2	.01	.01	...	...	.01	mg/l as N
NO3	9.9	11.2	11.6	.5	9.25	mg/l as N
NH3	.01	<.1	<.1	.1	<.01	mg/l as N
F	.18	.14	.16	.17	.1	mg/l
PO4	.02	<.01	.02	.56	.04	mg/l as P
BOD	...	...	...	...	...	mg/l as O
COD	...	...	...	...	<5	mg/l as O
EC	415	445	...	...	440	mhos/cm
SS	17	<1	...	...	<1	mg/l

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N. INLET TO KINGHORN LOCH
statistical appraisal - for 30/5/83 to 27/9/84

	samples	maximum	minimum	mean	std.dev.	n20	n10	n5	
flow	44	66	1.65	13.2716	12.4348	84	337	1349	l/s
temp	41	12.5	.5	8.13415	2.51004	9	37	146	C
pH	49	8.2	7.2	7.98573	.203712	16	64	399	
tot Ca	1	.1	.1	.05	...	...	...	...	mg/l
dis Ca	47	58.5	23.4	41.4766	7.19365	3	12	46	mg/l
tot Mg	1	.2	.2	.2	...	...	...	...	mg/l
dis Mg	47	32.5	15.4	18.7102	2.3191	1	6	24	mg/l
Na	48	899	11.9	39.3313	126.915	1000	4000	16000	mg/l
K	48	2.32	.12	.647292	.375111	32	129	516	mg/l
tot Al	6	356	<.1	59.6667	145.174	569	2274	9097	mg/l
dis Al	45	.8	<.1	.148	.152845	102	410	1639	mg/l
dis Fe	44	.25	<.01	.046363	.054113	131	523	2093	mg/l
tot As	6	.6	<.005	.103	.243489	537	2147	8587	mg/l
tot V	6	1.3	<.1	.258333	.51031	375	1499	5996	mg/l
tot alk	4	150	125	136.25	11.0868	1	3	10	mg/l CaCO3
dis alk	49	155	100	131.531	14.296	1	5	18	mg/l CaCO3
Cl	45	35	13	27.3333	3.50325	2	6	25	mg/l
SO4	45	28	9.6	18.0534	3.77015	4	17	67	mg/l as S
dis SiO2	48	6.29	.789999	4.58396	.885876	4	14	57	mg/l as Si
B	44	.23	<.025	.065284	.039081	34	138	551	mg/l
NO2	43	.08	.005	.013023	.014063	112	448	1792	mg/l as N
NO3	49	12.8	<.1	8.5755	2.65961	9	37	148	mg/l as N
NH3	48	.3	<.01	.064062	.054749	70	281	1122	mg/l as N
F	40	.44	.1	.173125	.065081	14	54	217	mg/l
PO4	45	.56	<.01	.034222	.081714	548	2190	8761	mg/l as P
BOD	1	.9	.9	.9	...	...	...	....	mg/l as O
COD	1	5	5	2.5	...	...	...	...	mg/l as O
EC	48	470	305	420.312	34.3084	1	3	10	mhos/cm
SS	48	17	<1	4.38542	4.27666	91	365	1461	mg/l

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N. INLET TO KINGHORN LOCH
statistical appraisal — for 30/5/83 to 27/9/84

	samples	maximum	minimum	mean	std.dev.	n20	n10	n5	
tot Ca	...	...	...	...	...	...	...	...	mg/s
dis Ca	43	2501.4	65.505	555.564	514.437	82	329	1318	mg/s
tot Mg	...	...	...	...	...	...	...	...	mg/s
dis Mg	43	1020.36	27.06	245.661	213.499	73	290	1161	mg/s
Na	43	1870.5	28.875	283.707	323.085	125	498	1993	mg/s
K	43	116.16	.857999	10.8142	20.1567	334	1335	5338	mg/s
tot Al	3	9.13	1.97	5.58833	...	...	...	...	mg/s
dis Al	40	17.4	.329999	2.22118	3.50927	240	959	3836	mg/s
dis Fe	41	12.54	<.049001	.929902	2.27267	574	2295	9178	mg/s
tot As	2	.0665	.0664	.049824	...	...	...	...	mg/s
tot V	2	1.33	.83	.539999	...	...	...	...	mg/s
tot alk	2	1729	1245	1487	...	...	...	...	mg/s CaCO3
dis alk	44	6600	173.25	1685.45	1379.07	64	257	1029	mg/s CaCO3
Cl	40	1914	47.85	397.774	389.648	92	369	1474	mg/s
SO4	43	877.8	30.195	229.387	198.354	72	287	1149	mg/s as S
dis SiO2	43	258.06	6.6825	59.0773	50.9846	72	286	1144	mg/s as Si
B	41	4.35	.041249	.744323	.709459	87	349	1396	mg/s
NO2	40	.975999	<.0165	.165656	.206142	149	595	2380	mg/s as N
NO3	44	752.4	<.830001	128.836	147.358	126	503	2010	mg/s as N
NH3	43	6.6	<.040001	.831918	1.15559	185	741	2965	mg/s as N
F	37	15.18	.280499	2.42868	2.73384	122	487	1947	mg/s
PO4	40	2.64	.049499	.311775	.457362	207	827	3307	mg/s as P
BOD	1	11.61	11.61	11.61	...	...	...	...	mg/s as O
COD	1	20	20	10	...	...	...	...	mg/s as O
SS	44	924	<4	82.8705	181.037	458	1833	7333	mg/s

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TABLE A.4. Chemical analysis of the west inlet to Kinghorn Loch (at roadside dam) for the period 14-6-1983 to 27-9-1984; including statistical appraisal.

WEST INLET TO KINGHORN LOCH for 14/6/83 to 1/8/83

date	14/6/83	22/6/83	28/6/83	1/7/83	8/7/83	10/7/83	18/7/83	26/7/83	1/8/83	
time	1815	1900	1630	0900	0745	1600	0815	0830	1610	
flow	.8	<.8	<.8	.2	.2	.18	.2	.2	.3	l/s
temp	10	13	11	9.5	12	12	...	12	11.5	C
pH	8.4	8.3	8.1	8.1	8.2	8.1	8.2	8.2	8.1	
dis Ca	38.1	35.5	31.5	33.6	44.4	45.6	45	52.3	51.3	mg/l
dis Mg	44.4	27.5	29.3	31.7	27.6	27.1	28.2	27.9	28.3	mg/l
Na	108.1	101	108.3	107.4	113.9	103.4	109.6	118	118.8	mg/l
K	2.99	2.67	2.98	3.06	3.1	2.6	2.9	3.4	3.4	mg/l
tot Al	...	...	...	...	...	...	...	...	...	mg/l
dis Al	.3	.6	.2	.1	.2	.2	.1	...	...	mg/l
dis Fe	.04	<.01	<.01	.01	<.05	<.05	<.05	<.05	<.05	mg/l
tot As	...	...	...	...	...	...	...	...	...	mg/l
tot V	...	...	...	...	...	...	...	...	...	mg/l
tot alk	...	...	...	...	...	...	...	...	...	mg/l
dis alk	275	285	275	270	275	280	265	275	260	mg/l CaCO3
Cl	59	65	52	53	53	48	50	50	48	mg/l CaCO3
SO4	54.3	47.3	36.3	47.3	50.6	49.3	65	54.6	65	mg/l
dis SiO2	2.33	2.47	2.02	2.33	2.33	3.21	3.03	3.17	2.56	mg/l as S
B	.15	.15	.15	.15	.15	.25	.2	.25	.2	mg/l as Si
NO2	.13	.05	.07	.08	.08	.04	.05	.06	.04	mg/l
NO3	3.5	2.9	2.7	2.6	2.4	2.3	2.1	1.8	1.8	mg/l as N
NH3	<.1	.3	.2	.2	.2	.2	.2	.1	.1	mg/l as N
F	.62	.69	.56	.6	.56	.52	1.6	1.3	1	mg/l as N
PO4	.06	<.01	.03	.03	.03	<.01	<.01	.05	.05	mg/l
sulphide	...	...	...	...	...	...	...	...	...	mg/l as P
COD	...	...	...	...	...	...	...	...	...	mg/l as S
DO	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	mg/l as O
EC	780	760	780	800	800	840	820	780	780	% as O
SS	3	6	6	2	8	2	4	4	6	mhos/cm
										mg/l

WEST INLET TO KINGHORN LOCH for 6/8/83 to 1/10/83

date	6/8/83	8/8/83	20/8/83	1/9/83	12/9/83	20/9/83	24/9/83	28/9/83	1/10/83	
time	1730	1040	2025	1100	0915	0730	0735	1130	0925	
flow	.2	...	.2	0	.15	.1	.1	...	.2	l/s
temp	13.5	...	13.5	...	8.5	9	10	...	10	C
pH	7.8	8.1	8.2	...	8	7.9	8	7.8	7.7	
dis Ca	11.9	...	11.4	...	44.8	48.7	52.3	39.6	43.5	mg/l
dis Mg	22.1	...	21.7	...	27.1	28.3	28.1	24.9	26.4	mg/l
Na	108.1	...	108.2	...	113.6	119.5	132.5	120	118.6	mg/l
K	2.9	...	2.7	...	2.96	3.36	3.6	2.8	3.49	mg/l
tot Al	...	<.1	...	...	...	...	...	.3	...	mg/l
dis Al	.1	.1	.1	...	.2	.1	.1	.3	.1	mg/l
dis Fe	<.05	...	<.05	...	<.05	<.05	.05	.02	.04	mg/l
tot As	...	.05	...	...	...	...	...	.11	...	mg/l
tot V	...	<.1	...	...	...	...	...	.2	...	mg/l
tot alk	...	270	...	...	...	...	...	310	...	mg/l CaCO3
dis alk	290	270	300	...	290	295	305	285	315	mg/l CaCO3
Cl	48	...	50	...	60	59	49	54	50	mg/l
SO4	68	...	69.6	...	47.3	50	50	...	56.6	mg/l as S
dis SiO2	3.31	...	3.31	...	3.26	3.63	3.82	2.23	3.73	mg/l as Si
B	.25	...	...	...	.25	.3	.28	.32	.25	mg/l
NO2	.04	...	.05	...	.03	.05	.04	.02	.02	mg/l as N
NO3	1.7	...	1.5	...	<.1	1	.9	.5	.9	mg/l as N
NH3	.1	...	.2	...	.1	.2	.2	.03	.3	mg/l as N
F	.7	...	.66	...	.58	.38	.5	...	.85	mg/l
PO4	.04	...	.08	...	.05	.06	.03	.02	.07	mg/l as P
sulphide	...	...	...	...	.04	.07	.04	...	.19	mg/l as S
COD	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	6.6	...	6.4	6.4	6.8	...	6.3	mg/l as O
DO	...	...	63.4	...	54.7	55.4	60.3	...	55.9	% as O
EC	740	740	790	...	830	840	880	900	810	mhos/cm
SS	3	1	2	...	4	1	3	7	3	mg/l

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WEST INLET TO KINGHORN LOCH for 9/10/83 to 27/11/83

date	9/10/83	20/10/83	25/10/83	2/11/83	7/11/83	9/11/83	19/11/83	23/11/83	27/11/83	
time	1640	0850	1815	0815	1710	1045	0820	0715	1535	
flow	.2	0	...	<.1	0	<.1	<.1	<.1	.2	l/s
temp	...	...	9	8	...	...	3.5	2	5.5	C
pH	8	...	8.1	7.9	...	7.6	7.6	7.7	7.9	
dis Ca	44	...	44.9	50.5	...	52.9	53.2	54.1	48.8	mg/l
dis Mg	25.9	...	24	27.1	...	27.4	28.6	28.5	27.3	mg/l
Na	112.6	...	105	108.1	...	106.6	105.7	104.1	108.6	mg/l
K	3.38	...	3.83	4.1	...	4.27	4.09	4.37	2.82	mg/l
tot Al	...	...	...	...	...	.1	...	...	...	mg/l
dis Al	.3	...	.4	.3	...	.4	<.1	.3	.1	mg/l
dis Fe	.13	...	<.01	.01	...	.07	<.01	<.01	<.01	mg/l
tot As	...	...	...	...	...	.06	...	...	...	mg/l
tot V	...	...	...	...	...	<.1	...	...	...	mg/l
tot alk	...	...	...	...	...	305	...	...	...	mg/l CaCO3
dis alk	320	...	305	315	...	305	310	305	320	mg/l CaCO3
Cl	49	...	51	49	...	49	54	54	...	mg/l
SO4	60	...	52	54.6	...	56	46.6	46.6	40	mg/l as S
dis SiO2	3.73	...	3.07	3.82	...	4.1	4.1	3.96	3.73	mg/l as Si
B	.25	...	.2	.2	...	.2	.17	.25	.2	mg/l
NO2	.02	...	.02	.05	...	.09	.04	.05	...	mg/l as N
NO3	1.1	...	2.5	1.5	...	.7	.5	.8	.9	mg/l as N
NH3	.1	...	.15	.04	...	.1	1.03	1.04	<.1	mg/l as N
F	.8	...	...	.49	...	.56	...	...	...	mg/l
PO4	.06	...	.02	.03	...	<.01	.1	.08	...	mg/l as P
sulphide	...	...	...	...	...	...	...	...	...	mg/l as S
COD	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	% as O
EC	810	...	850	800	...	840	820	820	720	mhos/cm
SS	3	...	4	9	...	2	...	...	<1	mg/l

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WEST INLET TO KINGHORN LOCH for 1/12/83 to 6/2/84

date	1/12/83	12/12/83	24/12/83	28/12/83	1/1/84	17/1/84	29/1/84	1/2/84	6/2/84	
time	1715	1440	0...	1430	1350	1015	1550	1000	1300	
flow	.2	.1	...	1.6	...	...	1.6	14.2	2.3	l/s
temp	5.5	5.5	...	8	6	3.5	6	5	5.5	C
pH	8	7.8	7.7	8	8	8.4	7.9	8.2	8.2	
dis Ca	50.1	48.7	49	55.7	51.5	31.5	51.5	52.6	62.7	mg/l
dis Mg	27.1	27.6	28.4	30.3	29.3	31.5	35.3	35.6	43.4	mg/l
Na	107.2	108.1	154.8	129.3	129.3	406	221.6	287	388	mg/l
K	2.82	3	6.81	6.67	4.95	12.86	8.01	8.61	17.75	mg/l
tot Al	...	...	...	...	...	...	...	...	...	mg/l
dis Al	.3	.3	.5	.2	.2	.2	.1	<.1	.3	mg/l
dis Fe	<.01	.07	.05	.04	.08	.1	.14	.06	.05	mg/l
tot As	...	...	...	...	...	...	...	...	...	mg/l
tot V	...	...	...	...	...	...	...	...	...	mg/l
tot alk	...	...	...	...	...	...	...	...	...	mg/l CaCO3
dis alk	310	310	305	300	275	430	360	410	460	mg/l CaCO3
Cl	...	...	57	60	55	70	62	75	70	mg/l
SO4	40	48	112.3	111.3	91	246.6	166	166	270	mg/l as S
dis SiO2	3.63	3.87	3.35	3.35	3.35	2.7	3.31	2.7	2.98	mg/l as Si
B	.2	.2	.25	.25	<.025	.55	.325	.3	.5	mg/l
NO2	...	...	.04	.04	.1	.04	.025	.03	.06	mg/l as N
NO3	.9	.7	3.5	3.5	4	2.3	5.4	3.6	5	mg/l as N
NH3	<.1	.03	<.1	.2	<.1	.1	.07	1.06	.1	mg/l as N
F	...	...	...	...	.78	1.8	1.1	1.5	2.2	mg/l
PO4	...	...	.02	.03	.05	.1	.05	.04	.08	mg/l as P
sulphide	...	...	...	...	...	...	...	...	...	mg/l as S
COD	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	% as O
EC	740	800	800	870	940	1850	1360	1550	1700	mhos/cm
SS	<1	4	4	6	2	2	11	4	6	mg/l

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WEST INLET TO KINGHORN LOCH for 20/2/84 to 27/9/84

date	20/2/84	22/2/84	29/2/84	6/3/84	11/3/84	21/3/84	28/3/84	16/4/84	27/9/84	
time	0730	1535	1030	1040	1750	1015	1110	1945	0920	
flow	2.3	2.8	2.9	2.2	.3	.2	.2	<.1	<.1	l/s
temp	6	6.5	6.5	7	7	4.5	6.5	7.5	12	C
pH	8.4	8.4	8.7	9	8.5	8.1	8.1	8.5	8.5	
dis Ca	30.9	33.7	17.7	14.4	27.9	46.8	46.8	27.9	25.8	mg/l
dis Mg	27.79	25.52	21.13	20.12	24.31	19.65	30.13	24.2	23.1	mg/l
Na	545	476	390	308	233	226	185.3	173	416	mg/l
K	18.75	16.65	16.04	7.04	6.43	6.3	7	3.53	9	mg/l
tot Al	...	...	1.3	...	...	...	...	...	...	mg/l
dis Al	.6	.5	1.2	3.6	1.7	1.3	.6	.4	...	mg/l
dis Fe	.01	.08	.04	.02	.03	.07	.05	...	<.05	mg/l
tot As	...	...	...	...	...	...	...	...	...	mg/l
tot V	...	...	...	...	...	...	...	...	...	mg/l
tot alk	...	...	...	...	...	...	...	...	...	mg/l CaCO3
dis alk	525	500	490	460	410	310	280	325	420	mg/l CaCO3
Cl	65	61	64	59	58	52	60	53	52	mg/l
SO4	288.3	250	216.6	124.6	119.3	73	123.3	80.3	109.3	mg/l as S
dis SiO2	2.05	2.05	1.63	1.49	2.33	3.12	3.03	2	2.33	mg/l as Si
B	.6	.5	.475	.35	.5	.25	.35	.25	.35	mg/l
NO2	.11	.1	.21	.17	.17	.02	.03	.03	.06	mg/l as N
NO3	3.6	3.7	3.5	3.35	3.5	2.8	5.4	2.2	.8	mg/l as N
NH3	.1	<.1	.1	.02	.12	.14	<.01	<.1	.1	mg/l as N
F	3.1	2.9	3	2.5	1.8	.6	.9	1.1	2.2	mg/l
PO4	.09	.1	.06	.09	.05	.03	.02	.01	.4	mg/l as P
sulphide	...	...	...	...	...	...	...	...	...	mg/l as S
COD	...	...	...	...	...	...	...	...	19	mg/l as O
DO	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	% as O
EC	2430	2160	2050	1400	1210	940	1150	580	1160	mhos/cm
SS	1	1	2	6	5	<1	<1	1	2	mg/l

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WEST INLET TO KINGHORN LOCH
statistical appraisal - for 14/6/83 to 27/9/84

	samples	maximum	minimum	mean	std.dev.	n20	n10	n5	
flow	39	14.2	0	.908461	2.33938	637	2547	10190	l/s
temp	36	13.5	2	8.11111	3.07318	14	55	221	C
pH	42	9	7.6	8.10476	.295578	34	134	839	
dis Ca	41	62.7	11.4	41.539	12.6591	9	36	143	mg/l
dis Mg	41	44.4	19.65	27.8988	5.01465	3	12	50	mg/l
Na	41	545	101	181.544	119.939	42	168	671	mg/l
K	41	18.75	2.6	5.80463	4.42886	56	224	895	mg/l
tot Al	4	1.3	<.1	.4375	.585057	172	687	2748	mg/l
dis Al	39	3.6	<.1	.428205	.628154	207	827	3307	mg/l
dis Fe	40	.14	<.01	.038625	.033107	71	282	1129	mg/l
tot As	3	.11	.05	.073333	...	...	...	...	mg/l
tot V	3	.2	.1	.1	...	...	...	...	mg/l
tot alk	3	310	270	295	...	...	...	...	mg/l
dis alk	42	525	260	330.238	71.6101	5	18	72	mg/l CaCO3
Cl	38	75	48	55.9737	6.90671	1	6	23	mg/l CaCO3
SO4	40	288.3	36.3	95.0725	69.6343	52	206	824	mg/l
dis SiO2	41	4.1	1.49	2.98829	.708197	5	22	86	mg/l as S
B	40	.6	<.025	.274562	.124625	20	79	317	mg/l as Si
NO2	38	.21	.02	.061973	.045195	51	204	817	mg/l
NO3	41	5.4	<.1	2.30244	1.39888	35	142	567	mg/l as N
NH3	41	1.06	<.01	.185	.254735	182	728	2913	mg/l as N
F	32	3.1	.38	1.20156	.815554	44	177	708	mg/l as N
PO4	38	.4	<.01	.056052	.064011	125	501	2004	mg/l
sulphide	4	.19	.04	.085	.071414	68	271	1085	mg/l as P
COD	1	19	19	19	...	...	...	...	mg/l as S
DO	5	6.8	6.3	6.5	.199992	0	0	1	mg/l as O
DO	5	63.4	54.7	57.94	3.75819	0	2	6	mg/l as O
EC	42	2430	580	1024.29	432.35	17	68	274	% as O
SS	40	11	<1	3.55	2.5161	48	193	772	mhos/cm
									mg/l

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WEST INLET TO KINGHORN LOCH
statistical appraisal - for 14/6/83 to 27/9/84

	samples	maximum	minimum	mean	std.dev.	n20	n10	n5		
dis Ca	36	746.92	1.29	42.5269	125.193	832	3329	13317	mg/s	
dis Mg	36	505.52	1.155	30.935	85.1161	727	2908	11633	mg/s	
Na	36	4075.4	5.205	295.192	747.375	616	2463	9850	mg/s	
K	36	122.262	.1765	9.94652	23.7785	549	2196	8782	mg/s	
tot Al	2	3.77	.005	1.8875	...	...	...	...	mg/s	
dis Al	33	7.92	<.005001	.544802	1.48423	713	2851	11405	mg/s	
dis Fe	35	.852	<.000501	.052285	.150125	792	3167	12668	mg/s	
tot As	1	.003	.003	.003	...	...	...	...	mg/s	
tot V	1	.005	.005	.0025	...	...	...	...	mg/s	
tot alk	1	15.25	15.25	15.25	...	...	...	...	mg/s	CaCO3
dis alk	36	5822	15.25	405.872	1017.75	604	2416	9662	mg/s	CaCO3
Cl	33	1065	2.45	70.5967	187.31	676	2704	10817	mg/s	
SO4	36	2357.2	2.33	167.207	429.074	632	2530	10119	mg/s	as S
dis SiO2	36	38.34	.1	2.50948	6.43132	631	2523	10093	mg/s	as Si
B	35	4.26	.0085	.3554	.8028	490	1960	7841	mg/s	
NO2	33	.608999	.0015	.076536	.145986	349	1398	5591	mg/s	as N
NO3	36	51.12	<.015	3.48546	8.88337	624	2495	9982	mg/s	as N
NH3	36	15.052	<.002	.479583	2.49945	2609	10435	41738	mg/s	as N
F	30	21.3	.0245	2.05354	4.47105	455	1821	7284	mg/s	
PO4	33	.567999	<.000501	.059474	.117728	376	1505	6021	mg/s	as P
sulphide	4	.038	.004	.01375	.016214	134	534	2137	mg/s	as S
COD	1	.95	.95	.95	...	...	...	...	mg/s	as O
DO	5	1.32	.64	.972	.316101	10	41	163	mg/s	as O
DO	5	12.68	5.54	8.727	3.13635	12	50	198	%	as O
SS	34	56.8	.05	4.14883	10.2741	589	2356	9423	mg/s	

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TABLE A.5. Chemical analysis of Kinghorn Loch at outlet sluice for the period 4-1-1981 to 24-5-1983; including statistical appraisal.

KINGHORN LOCH AT OUTLET for 4/1/81 to 23/2/81

date	4/1/81	9/1/81	20/1/81	25/1/81	29/1/81	2/2/81	9/2/81	15/2/81	23/2/81	
time	1610	1130	1330	1155	1020	1115	1135	1730	1635	
flow	...	51	32	42	46	...	26	32	26	l/s
temp	4	4	.5	1.5	4	5	2	4	2	C
pH	9.8	9.9	9.7	9.7	9.5	9.3	9.7	9.6	9.7	
tot Ca	14.6	12.7	56.8	53.8	54.8	...	31.3	31	12.3	mg/l
dis Ca	...	...	...	...	...	...	...	...	...	mg/l
tot Mg	10.8	12.5	22.2	22.4	22.1	...	14.9	13.9	17.6	mg/l
dis Mg	...	...	...	...	...	...	...	...	...	mg/l
Na	238.1	230.8	249	234	235	...	213	223	216	mg/l
K	6	5.6	4	4	4	...	3.8	3.7	3.2	mg/l
tot Al	4.8	4	7.3	6.4	7.8	6.4	9	8.3	8.8	mg/l
dis Al	4	4.1	6.8	5.8	7.5	1.7	...	...	...	mg/l
tot Fe	.2	.1	.5	.4	<.1	...	...	...	...	mg/l
dis Fe	...	...	...	...	...	...	...	...	...	mg/l
tot As	.35	.36	.3	.32	.32	...	...	...	.31	mg/l
tot V	.7	.6	.6	.5	.5	...	...	...	.6	mg/l
tot alk	345	355	375	375	355	370	370	395	380	mg/l CaCO3
dis alk	345	350	385	365	365	365	370	395	365	mg/l CaCO3
Cl	72	67	44	45	39	...	23	24	25	mg/l
SO4	60	54.6	49.3	52	55	...	53	58.3	46.3	mg/l as S
dis SiO2	1.49	1.53	1.58	1.67	1.81	...	2.23	2.42	.93	mg/l as Si
B	.09	.09	.09	.08	.08	...	.1	.13	.08	mg/l
NO2	.32	.16	.04	.04	.05	...	.31	.32	.02	mg/l as N
NO3	2.8	3	3.6	4	3.15	...	8.5	3	8.8	mg/l as N
NH3	.7	.4	<.1	.1	.6	...	<.1	.2	.1	mg/l as N
F	1.4	1.9	2.1	2.1	1.9	...	.9	.7	1	mg/l
PO4	.04	.02	.09	.11	.05	...	.08	.07	.09	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	% as O
EC	735	770	840	800	740	860	845	875	790	mhos/cm
SS	7	6	7	5	8	13	13	28	25	mg/l
ash	...	...	...	...	...	...	...	...	...	mg/l
chl'phyll	...	...	...	...	...	...	...	...	...	ug/l

KINGHORN LOCH AT OUTLET for 27/2/81 to 26/4/81

date	27/2/81	9/3/81	14/3/81	21/3/81	29/3/81	30/3/81	9/4/81	20/4/81	26/4/81	
time	1050	1235	1120	1410	1825	1225	2005	2005	2005	
flow	18	32	65	58	58	...	26	26	26	l/s
temp	2	5	6	5.5	7	8	9	11	9	C
pH	9.7	9.8	9.8	9.5	9.5	9.5	9.6	9.6	9.6	
tot Ca	4	14.2	5	.3	3.7	...	6.4	3.6	4.6	mg/l
dis Ca	...	...	...	.2	2.1	...	4.6	1.8	4.4	mg/l
tot Mg	16.5	21.1	17.3	2.8	14.1	...	13.5	12.3	12.4	mg/l
dis Mg	...	...	...	1.6	2.1	...	12.2	10.9	10.5	mg/l
Na	218	222	225	223	219	...	218	222	225	mg/l
K	3.4	3.3	3.3	3.3	3.8	...	3.4	4	3.8	mg/l
tot Al	9.1	11.7	6.6	6.5	10.2	...	12.7	10.3	10.2	mg/l
dis Al	...	...	...	5.9	5.5	...	11.3	10.5	10.1	mg/l
tot Fe	...	...	...	...	...	...	...	.1	.2	mg/l
dis Fe	...	...	...	...	...	...	...	...	...	mg/l
tot As	...	...	.31	...	...	.28	...	...	.32	mg/l
tot V	...	...	.6	...	...	.6	...	...	.5	mg/l
tot alk	390	375	385	325	330	390	360	370	370	mg/l CaCO3
dis alk	380	380	350	325	325	350	370	360	355	mg/l CaCO3
Cl	24	40	38	38	39	...	36	39	39	mg/l
SO4	44.3	35.6	36	41.8	36.3	...	36.3	56.6	58.6	mg/l as S
dis SiO2	1.3	1.49	1.91	.74	.6	...	1.63	1.49	1.39	mg/l as Si
B	.1	.13	.09	.1	.1	...	.15	.15	.14	mg/l
NO2	.02	.05	.06	.22	.03	...	.04	.05	.07	mg/l as N
NO3	8.8	3.454	3.1	3.8	3.2	...	3.9	3.6	3.7	mg/l as N
NH3	.1	.02	.2	.3	.2	...	.2	.5	.3	mg/l as N
F	.8	1.25	1.3	2.1	2.1	...	.9	1.2	.9	mg/l
PO4	.07	.14	.07	.6	.05	...	.11	.09	.1	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	% as O
EC	760	820	740	820	820	850	800	840	820	mhos/cm
SS	16	36	15	69	65	16	13	12	15	mg/l
ash	...	...	...	...	...	...	...	...	...	mg/l
chl'phyll	...	...	...	...	...	...	...	...	21	ug/l

KINGHORN LOCH AT OUTLET for 2/5/81 to 9/7/81

date	2/5/81	23/5/81	1/6/81	9/6/81	13/6/81	21/6/81	28/6/81	1/7/81	9/7/81	
time	1550	1320	1735	1740	1115	2100	1635	1605	0950	
flow	26	46	18	18	18	26	18	18	5	l/s
temp	10	15	17	16	16	19	16	17	16	C
pH	9.7	9.7	9.8	9.8	9.8	10	9.9	10	9.7	
tot Ca	12.2	16	11.4	6.2	5.3	5	3.9	6.6	4.1	mg/l
dis Ca	6.7	13.1	5.7	6.1	3.4	2.5	2.5	3.5	2.4	mg/l
tot Mg	12.4	11.3	9.2	6.1	5.4	6.6	5.2	5.6	7.3	mg/l
dis Mg	9.6	9.1	3.5	5	3.8	1.4	4.4	5	5.4	mg/l
Na	189	189	151	210	194	196	197	195	210	mg/l
K	2.8	2.2	2.2	3	2.9	3	2.8	2.6	2.8	mg/l
tot Al	10.1	8.6	8	7.3	7.5	3.3	5.2	5.7	5.5	mg/l
dis Al	10.2	9.7	5.4	5.9	6.7	2.1	4.9	4.6	5.4	mg/l
tot Fe	<.1	.1	.2	.1	.1	.4	.2	.2	.1	mg/l
dis Fe	...	...	...	...	...	...	...	...	...	mg/l
tot As	...	...	...	...	.29	...	...	...	.36	mg/l
tot V	...	...	...	...	.3	...	...	...	.2	mg/l
tot alk	475	335	340	390	365	365	365	360	390	mg/l CaCO3
dis alk	365	335	340	320	350	365	375	360	...	mg/l CaCO3
Cl	37	39	38	...	...	36	35	31	37	mg/l
SO4	58	55.3	51.6	57.6	42.3	48.6	55.3	56.3	58	mg/l as S
dis SiO2	1.44	1.11	1.21	.74	.88	1.02	.88	.97	.74	mg/l as Si
B	.2	.09	.19	.15	.1	.1	.1	.1	.15	mg/l
NO2	.07	.06	.07	.01	<.01	.05	.06	<.01	.01	mg/l as N
NO3	3.6	2.4	2	.9	.7	.3	.7	.7	<.1	mg/l as N
NH3	.06	.3	.2	<.1	1.3	.3	.2	.1	1.6	mg/l as N
F	.96	.33	.32	.27	.27	1.25	1.25	1.6	1.7	mg/l
PO4	.07	.07	<.01	<.01	.03	.07	.08	.7	.1	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	% as O
EC	820	770	660	870	770	830	840	830	920	mhos/cm
SS	20	10	36	14	20	33	18	31	16	mg/l
ash	...	...	...	...	...	...	...	...	...	mg/l
chl'phyll	...	202	51	320	35	15	97	...	18	ug/l

KINGHORN LOCH AT OUTLET for 20/7/81 to 9/9/81

date	20/7/81	21/7/81	25/7/81	3/8/81	9/8/81	18/8/81	24/8/81	2/9/81	9/9/81	
time	1710	1300	1355	0915	1230	1800	1320	1810	0930	
flow	5	...	10	13	24	<5	18	<5	<5	l/s
temp	17.5	...	17	18	18	17	18	16	18	C
pH	9.9	9.8	10	10	9.8	9.7	9.8	9.8	9.7	
tot Ca	3.4	...	1.9	2.6	4.7	17.2	7.1	4.6	5.1	mg/l
dis Ca	2.4	...	2.7	2.7	1.2	1.5	1.2	1.6	1.4	mg/l
tot Mg	6.5	...	6.3	5.4	5.9	9.9	7	5.1	5.2	mg/l
dis Mg	5.3	...	<.1	5.7	5.2	4.6	4.6	4.4	4.7	mg/l
Na	207	...	178	223	244	226	248	240	250	mg/l
K	2.4	...	2	2.8	3.6	3.4	4	4	4	mg/l
tot Al	4.9	5.8	6.3	6.3	4.8	6.5	5.8	4.3	4.6	mg/l
dis Al	5.2	...	5.7	5.3	4.9	5.2	5	4.4	4.7	mg/l
tot Fe	.1	...	.1	<.1	<.1	.8	.1	<.1	<.1	mg/l
dis Fe	...	...	...	...	...	...	...	...	...	mg/l
tot As	...	...	...	.33	...	...	.33	...	...	mg/l
tot V	...	...	...	.4	...	...	.5	...	...	mg/l
tot alk	390	390	390	400	400	405	410	420	410	mg/l CaCO3
dis alk	...	355	390	400	400	405	410	420	410	mg/l CaCO3
Cl	35	...	37	32	34	32	30	37	39	mg/l
SO4	37.6	...	48	61.3	43.6	41.6	44.3	43.6	44.6	mg/l as S
dis SiO2	.88	...	.83	.93	.97	2.14	1.02	.27	.74	mg/l as Si
B	.15	...	.15	.15	.1	.15	.1	.1	.15	mg/l
NO2	.06	...	.05	.03	.02	<.01	.01	.18	.01	mg/l as N
NO3	.6	...	.5	.2	.2	.1	3.2	.2	.1	mg/l as N
NH3	.2	...	.3	.06	.31	.2	<.1	.1	.1	mg/l as N
F	2	...	3.5	4.8	.9	.46	.33	.26	.23	mg/l
PO4	.06	...	.1	.09	.42	.14	2.4	.15	...	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	11.5	...	7.6	mg/l as O
DO	...	...	...	...	...	...	121.6	...	80.3	% as O
EC	780	800	1040	840	780	760	815	800	760	mhos/cm
SS	9	20	6	6	7	50	33	12	14	mg/l
ash	...	...	...	...	...	...	...	...	...	mg/l
chl'phyll	<10	35	<10	...	<10	...	...	...	32	ug/l

KINGHORN LOCH AT OUTLET for 15/9/81 to 1/11/81

date	15/9/81	16/9/81	24/9/81	28/9/81	5/10/81	12/10/81	20/10/81	30/10/81	1/11/81	
time	1005	1720	1415	1750	1420	0930	1510	1530	0935	
flow	...	<5	<5	26	<5	5	32	32	5	l/s
temp	15	15	15	14	11	7	8	6	6	C
pH	9.5	9.6	9.7	9.7	9.7	9.8	10.1	9.9	9.9	
tot Ca	...	3.6	4.8	5.1	7.5	8.7	7.4	5.8	5.5	mg/l
dis Ca	...	4.1	4.5	5.3	1.6	2.7	2.6	3.4	3.7	mg/l
tot Mg	...	4.8	4.7	5.3	5.9	8.9	2.6	8.3	8.1	mg/l
dis Mg	...	5.4	4.7	7.1	5.5	8.9	8.3	8.5	7.4	mg/l
Na	...	264	264	277	286	276	291	292	295	mg/l
K	...	4.2	4.6	3.4	2.8	3.7	4	4	4	mg/l
tot Al	4	4.5	5.5	6.4	7.1	8.3	8.1	8.4	7.8	mg/l
dis Al	...	4.5	5.5	5.9	7.1	7.3	8.1	8.6	7.9	mg/l
tot Fe	...	.04	.08	.05	.04	.1	.1	<.1	<.1	mg/l
dis Fe	...	...	...	.05	.04	...	...	...	...	mg/l
tot As	.3	...	...	...	...	...	...	.32	...	mg/l
tot V	.4	...	...	...	...	...	...	.3	...	mg/l
tot alk	420	430	455	575	495	510	525	535	535	mg/l CaCO3
dis alk	420	420	450	575	495	510	525	535	535	mg/l CaCO3
Cl	...	41	40	41	39	35	32	31	32	mg/l
SO4	...	45.3	49.3	47.3	45.3	48	48	48	48	mg/l as S
dis SiO2	...	.93	.88	.88	1.02	1.3	1.02	.97	1.07	mg/l as Si
B	...	.1	.95	.7	.05	.15	.1	.1	.1	mg/l
NO2	...	<.01	<.01	.01	.02	.02	.04	<.01	<.01	mg/l as N
NO3	...	<.1	<.1	.25	.35	.8	.2	<.1	.1	mg/l as N
NH3	...	.03	.05	.04	.02	.2	.41	<.01	.24	mg/l as N
F	...	.25	.24	.19	1.9	1.8	1.6	1.8	1.7	mg/l
PO4	...	.05	.09	.17	.08	.12	.08	.18	.21	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	9.8	10.3	...	10.5	...	...	...	...	mg/l as O
DO	...	97.3	102.2	...	95.3	...	...	...	...	% as O
EC	820	730	810	845	730	1120	1030	1010	1010	mhos/cm
SS	34	5	11	5	14	14	12	25	21	mg/l
ash	...	...	...	...	...	...	...	...	...	mg/l
chl'phyll	...	<10	...	...	21	72	165	46	...	ug/l

KINGHORN LOCH AT OUTLET for 8/11/81 to 29/12/81

date	8/11/81	9/11/81	16/11/81	22/11/81	1/12/81	12/12/81	15/12/81	21/12/81	29/12/81	
time	1700	1410	1010	2010	0705	1100	2035	0950	1043	
flow	<5	<5	5	32	29	<5	40	<5	<5	l/s
temp	6	...	5.5	8	4	1	1	4	3	C
pH	9.9	9.9	10	10.1	10	9.7	9.9	9.2	9.3	
tot Ca	9.4	...	8.6	1.1	3.5	11.7	6	17.5	8.3	mg/l
dis Ca	3.5	...	6	1	.5	6.5	5.9	4.7	5	mg/l
tot Mg	10.8	...	8.9	7.5	10.8	16.8	8.6	11	8.6	mg/l
dis Mg	7.1	...	8.5	7.2	3	9.2	8.4	10.1	8.4	mg/l
Na	277	...	285	281	264	270.9	251	243	258	mg/l
K	3.8	...	3.9	3.4	3.2	3.2	3.5	3.5	3.9	mg/l
tot Al	7.1	9.3	8.6	8.7	6.8	7.8	8.7	6.9	7.2	mg/l
dis Al	7.1	...	8.3	8.7	5.2	7.5	8.5	6.9	7.2	mg/l
tot Fe	.3	...	<.05	.1	.1	<.05	<.05	<.05	<.05	mg/l
dis Fe	...	...	...	<.1	.1	.05	<.05	.07	<.05	mg/l
tot As	...	.42	...	...	...	...	...	.45	...	mg/l
tot V	...	.6	...	...	...	...	...	.6	...	mg/l
tot alk	525	520	555	535	470	435	460	400	455	mg/l CaCO3
dis alk	525	515	555	535	470	435	...	400	455	mg/l CaCO3
Cl	39	39	36	39	33	38	37	37	36	mg/l
SO4	48	...	47.3	47.3	53	46	47.7	50.3	48.6	mg/l as S
dis SiO2	1.25	...	1.35	1.21	1.81	1.16	1.67	2.61	2.65	mg/l as Si
B	.1	...	.1	.1	.05	.05	.1	.1	.05	mg/l
NO2	.05	<.01	<.01	.09	.14	.16	.18	.21	.18	mg/l as N
NO3	.3	<.1	.1	.9	8	2.6	1.9	2.5	1.9	mg/l as N
NH3	.3	<.01	.4	.3	.73	.53	.02	.8	.3	mg/l as N
F	1.6	...	1.5	.94	1.2	1	1.2	1.2	1.3	mg/l
PO4	.16	...	.17	.21	.18	.11	.11	.2	.1	mg/l as P
BOD	...	2.2	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	% as O
EC	1070	1550	1080	855	750	810	780	795	875	mhos/cm
SS	27	45	23	21	24	17	17	3	8	mg/l
ash	...	...	...	...	...	...	...	...	...	mg/l
chl'phyll	22	...	36	14	88	67	15	88	...	ug/l

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KINGHORN LOCH AT OUTLET for 1/1/82 to 10/3/82

date	1/1/82	10/1/82	19/1/82	26/1/82	1/2/82	9/2/82	21/2/82	1/3/82	10/3/82	
time	0950	1250	0900	1800	1310	1410	1725	0810	1815	
flow	13	68	55	56	53	37	18	40	32	l/s
temp	2	.5	2	4	4	4.5	3	4	4	C
pH	9.6	9.9	9.7	9.9	9.9	9.9	10	10.1	10.1	
tot Ca	5.7	14.9	17.4	11.5	...	...	...	...	...	mg/l
dis Ca	5.8	7.8	15.7	7	4.5	4.9	3.5	.9	.7	mg/l
tot Mg	8.2	11.5	14	21.2	...	...	...	...	...	mg/l
dis Mg	8.4	11.5	14.5	19	8.7	9.3	3.2	7.7	10	mg/l
Na	250	217	160	227.8	254	242	280	276.6	264.8	mg/l
K	3.67	3.4	2.69	3.2	3.5	3.5	3.8	4.1	2.73	mg/l
tot Al	7.4	7.3	5.7	6.9	...	...	...	...	...	mg/l
dis Al	7.2	7.2	5.2	6.9	5	5.6	5.6	7.7	8.3	mg/l
tot Fe	<.05	<.05	<.05	.4	...	...	...	...	...	mg/l
dis Fe	<.05	<.05	<.05	...	<.05	<.05	<.05	.07	<.05	mg/l
tot As	...	...	.17	...	...	...	...	...	...	mg/l
tot V	...	...	.2	...	...	...	...	...	...	mg/l
tot alk	460	395	295	420	...	...	...	...	...	mg/l CaCO3
dis alk	460	380	295	420	465	435	475	495	520	mg/l CaCO3
Cl	36	34	34	34	34	34	39	42	38	mg/l
SO4	55	44.3	36	45	44.3	47.3	45	45.6	47.6	mg/l as S
dis SiO2	1.07	.55	1.72	1.49	1.02	1.39	.6	.88	.74	mg/l as Si
B	.075	.075	.075	.075	.1	.025	.075	.1	.1	mg/l
NO2	.18	.12	.09	.14	.18	.2	.27	.24	.25	mg/l as N
NO3	1.8	3.6	5.1	3.2	2.6	3.2	3.4	3	3.8	mg/l as N
NH3	.2	.4	.2	.4	.2	.3	.1	.2	.4	mg/l as N
F	1.5	1.3	1	.17	.9	.96	.9	.76	.92	mg/l
PO4	.11	.07	.06	.11	.17	.08	.06	.1	.07	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	12.1	...	...	...	...	...	...	mg/l as O
DO	...	...	87.5	...	...	...	...	...	...	% as O
EC	780	820	660	...	1030	1040	1080	1020	1060	mhos/cm
SS	12	12	9	5	16	56	40	26	28	mg/l
Ash	...	...	...	...	...	...	...	...	...	mg/l
chl'phyll	...	12	...	...	...	22	25	52	18	ug/l

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KINGHORN LOCH AT OUTLET for 14/3/82 to 11/5/82

date	14/3/82	18/3/82	27/3/82	1/4/82	11/4/82	15/4/82	26/4/82	1/5/82	11/5/82	
time	0955	1455	1845	1005	1730	2000	1925	1640	1050	
flow	28	24	26	26	46	49	<5	...	5	l/s
temp	4.5	...	7	6.5	7	...	9.5	10	...	C
pH	10	10.1	10.1	10.2	10.4	10.2	9.9	10.4	10.5	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	.7	3.7	2.5	2.4	.8	1.1	<.5	<.5	1.6	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	7.1	4.5	1.3	1.1	.21	.78	1.76	.65	.7	mg/l
Na	276.2	284.4	303	291.6	280	284.2	240.4	279	261.9	mg/l
K	3.34	3.9	4.1	4	3.78	3.75	2.71	2.96	3.5	mg/l
tot Al	...	10.3	...	...	...	...	...	...	5	mg/l
dis Al	7.7	7.2	5.7	6.1	5	5.4	2.1	4.6	...	mg/l
tot Fe	...	...	...	...	...	...	...	...	...	mg/l
dis Fe	<.05	<.05	<.05	<.05	.06	.24	.21	.14	<.05	mg/l
tot As	...	.35	...	...	.36	...	...	...	.19	mg/l
tot V	...	..6	...	...	.5	...	...	...	.5	mg/l
tot alk	...	515	...	...	...	...	...	...	540	mg/l CaCO3
dis alk	500	500	465	475	480	485	455	515	540	mg/l CaCO3
Cl	37	45	41	43	38	38	43	39	38	mg/l
SO4	46.6	47.6	49.6	40	40	39	44	38.3	45.3	mg/l as S
dis SiO2	1.3	1.07	1.21	1.3	1.11	.88	1.11	1.02	1.04	mg/l as Si
B	.1	.08	.09	.09	.09	.09	.09	<.05	.17	mg/l
NO2	.26	.3	.31	.24	.13	.2	.19	.15	.02	mg/l as N
NO3	2.7	2.7	1.9	1.4	.2	.8	1.6	.6	<.1	mg/l as N
NH3	.7	.7	.9	.55	<.1	<.1	.7	<.1	1.1	mg/l as N
F	.74	.8	.92	.96	2	2.1	1.9	1.65	1.4	mg/l
PO4	.12	.1	.2	.05	.08	.07	.11	.08	.2	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	% as O
EC	1060	1000	1020	1020	1100	1085	810	1140	1240	mhos/cm
SS	50	41	78	72	88	83	36	63	51	mg/l
ash	...	...	...	...	...	...	...	...	4	mg/l
chl'phyll	194	72	34	88	261	194	302	115	96	ug/l

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KINGHORN LOCH AT OUTLET for 18/5/82 to 19/7/82

date	18/5/82	26/5/82	1/6/82	7/6/82	16/6/82	23/6/82	1/7/82	8/7/82	19/7/82	
time	1305	1010	0720	1615	1610	1610	0750	0855	2105	
flow	60	55	<5	58	<5	<5	<5	80	<5	l/s
temp	14	14.5	16	21	13.5	13	14	16	18	C
pH	10.3	10.5	...	10.3	9.9	10.2	9.9	10.2	9.9	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	1.8	.8	...	1.7	1.4	8.9	1.5	2.7	3.4	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	.71	.2	...	.2	1.3	1.6	.4	1	1.1	mg/l
Na	243	251.5	...	240.7	233.8	258.1	267.3	266.7	270.2	mg/l
K	3.2	3.5	...	3.4	3.1	3.6	3.7	4	4.1	mg/l
tot Al	...	...	...	...	...	...	...	...	...	mg/l
dis Al	4.6	4.1	...	4.3	4.7	6.8	5.8	6.9	7.7	mg/l
tot Fe	...	...	...	...	...	...	...	...	...	mg/l
dis Fe	<.05	.08	...	.35	.11	.04	.03	.04	.06	mg/l
tot As	...	...	...	.33	...	...	...	...	...	mg/l
tot V	...	...	...	.3	...	...	...	...	...	mg/l
tot alk	...	...	...	490	495	535	...	...	...	mg/l CaCO3
dis alk	515	505	...	480	470	480	475	500	535	mg/l CaCO3
Cl	42	38	...	39	42	41	39	39	39	mg/l
SO4	41.6	45	...	45	48.6	...	...	...	30.6	mg/l as S
dis SiO2	.62	.86	...	1.07	1.07	1.04	.97	.83	1.07	mg/l as Si
B	.1	.1	...	.1	.075	.1	.05	.05	.05	mg/l
NO2	<.01	<.01	...	<.01	.01	.01	<.01	.07	.07	mg/l as N
NO3	<.1	<.1	...	<.1	.1	.1	<.1	<.1	.1	mg/l as N
NH3	<.1	<.1	...	.2	.4	.07	.7	.13	.5	mg/l as N
F	1.9	2.1	...	2.1	2	2.1	1.45	1.4	1.3	mg/l
PO4	.1	.07	...	.08	.1	.17	.08	.1	.09	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	% as O
EC	1150	1160	...	1040	1120	1130	1190	1030	1060	mhos/cm
SS	46	61	...	50	33	40	34	19	10	mg/l
ash	7	...	...	...	...	...	...	...	...	mg/l
chl'phyll	82	221	...	...	...	31	21	16	...	ug/l

KINGHORN LOCH AT OUTLET for 26/7/82 to 12/9/82

date	26/7/82	1/8/82	4/8/82	12/8/82	19/8/82	22/8/82	1/9/82	5/9/82	12/9/82	
time	2155	1230	1145	1745	1755	1740	1205	1730	1200	
flow	<5	<5	<5	<5	<5	<5	>50	<5	<5	l/s
temp	19	19	...	16	14	15	14	10.2	15	C
pH	9.7	10.1	10.1	10.2	10.1	10.2	10.3	10.1	10.4	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	10.7	2.9	2.3	2.5	3.6	2.6	2.7	3.4	1.7	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	3.1	.9	1.2	1.4	15.7	2.6	.7	.9	<.1	mg/l
Na	274	277.2	273.6	277.7	283	288	287	335	326.6	mg/l
K	4.4	4.2	3.9	4	5.5	4	4.2	4.9	5.1	mg/l
tot Al	...	...	6.5	...	...	...	...	...	...	mg/l
dis Al	7.4	7.7	8.2	7.7	9.4	10.6	9.5	10.6	9.7	mg/l
tot Fe	...	...	...	...	...	...	...	...	...	mg/l
dis Fe	.42	.06	.07	.08	.13	.06	<.01	<.01	.1	mg/l
tot As	...	...	.34	...	...	.33	...	.34	...	mg/l
tot V	...	...	.6	...	...	.4	...	.5	...	mg/l
tot alk	...	...	...	...	...	...	...	...	...	mg/l
dis alk	545	570	565	580	570	625	595	595	615	mg/l CaCO3
Cl	40	37	39	36	37	40	38	37	38	mg/l CaCO3
SO4	30.3	31.8	20.2	30.4	42	39.6	44.3	45	36	mg/l
dis SiO2	...	1.02	1.02	.88	.93	1	.88	1.02	.88	mg/l as S
B	...	.05	.1	.1	.1	.25	.15	.15	.15	mg/l as Si
NO2	.05	.04	.04	.03	.03	.03	<.01	<.01	.01	mg/l
NO3	.2	.15	.2	.2	.2	.1	<.1	<.1	<.1	mg/l as N
NH3	.1	.29	.3	.2	.1	.1	<.1	<.1	.2	mg/l as N
F	1.3	1.3	1.6	1.7	1.4	1.5	1.7	1.3	1.4	mg/l as N
PO4	.2	.1	.06	.09	.07	.08	.12	.13	.1	mg/l
BOD	...	...	.5	...	...	...	...	...	...	mg/l as P
DO	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	mg/l as O
EC	1380	1160	1330	1160	1040	1180	1060	1020	1450	% as O
SS	15	6	9	26	14	20	33	31	49	mhos/cm
ash	...	...	...	...	...	...	...	...	...	mg/l
chl'phyll	<10	...	<10	25	23	40	...	...	21	mg/l
										ug/l

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KINGHORN LOCH AT OUTLET for 19/9/82 to 17/11/82

date	19/9/82	23/9/82	26/9/82	1/10/82	10/10/82	26/10/82	1/11/82	8/11/82	17/11/82	
time	1720	1150	1810	1810	1515	1640	0840	1230	1215	
flow	<5	...	<5	<5	18	<5	<5	<5	<5	l/s
temp	...	...	10.5	11	9.5	8	8	9	5.25	C
pH	10.4	10.3	10.5	10.5	10.3	10.2	9.7	10.3	10.3	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	1.6	...	2.4	2.7	7.5	1.4	1.9	4	4	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	.4	...	1.6	1.6	4.5	<.5	.6	3.2	1.3	mg/l
Na	310	...	312.2	290.8	272	293.3	271.8	289.7	247.4	mg/l
K	5.4	...	4.5	4.5	4.4	4.4	3.6	4.3	3.4	mg/l
tot Al	...	10.5	...	...	...	...	...	...	...	mg/l
dis Al	11.5	...	16.1	11.8	9.9	7.9	7.1	9.4	7.1	mg/l
tot Fe	...	...	...	...	...	...	...	...	...	mg/l
dis Fe	.11	...	.18	<.05	.16	.18	<.05	.05	.09	mg/l
tot As	...	.36	...	...	...	.38	...	...	...	mg/l
tot V	...	.5	...	...	...	.7	...	...	...	mg/l
tot alk	...	635	...	...	...	...	...	...	...	mg/l CaCO3
dis alk	635	635	650	660	550	590	555	610	590	mg/l CaCO3
Cl	39	...	39	39	38	37	39	37	37	mg/l
SO4	41.6	...	45	42.6	38.3	40.6	39.6	44.3	42	mg/l as S
dis SiO2	.97	...	1.16	1.11	1.77	1.35	1.53	1.63	.97	mg/l as Si
B	.1	...	.125	.125	.1	.125	.125	.15	.1	mg/l
NO2	<.01	...	.01	.01	.01	<.01	.07	.09	.19	mg/l as N
NO3	<.1	...	<.1	<.1	.05	.1	.6	.4	1.2	mg/l as N
NH3	.2	...	.01	.01	.01	.1	.1	.2	.4	mg/l as N
F	1.7	...	1.65	1.6	1.4	2.4	1.9	1.7	1.95	mg/l
PO4	.1	...	.13	.11	.2	.09	.21	.13	.14	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	% as O
EC	1255	1355	1150	1200	1220	1180	1200	1150	1110	mhos/cm
SS	31	27	43	31	25	65	26	26	26	mg/l
ash	...	...	...	...	...	...	...	...	...	mg/l
chl'phyll	16	11	42	121	76	...	40	15	31	ug/l

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KINGHORN LOCH AT OUTLET for 22/11/82 to 24/1/83

date	22/11/82	1/12/82	8/12/82	14/12/82	25/12/82	1/1/83	9/1/83	18/1/83	24/1/83	
time	1745	0950	1800	1245	1340	1530	1630	1400	0...	
flow	<5	60	...	...	...	...	...	...	...	l/s
temp	4	4	4	4	2	7.5	3	3	...	C
pH	10.4	10.1	10.1	10	10.1	10.1	10.1	10	...	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	1.7	2.5	3.9	4	2.6	2.5	7.2	6	...	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	.2	1.1	1.8	2.1	.9	1.1	7	8.2	...	mg/l
Na	290	274.6	249.3	235.1	266	265	264	255	...	mg/l
K	4.5	4.2	3.6	3.5	3.79	3.83	3.86	3.58	...	mg/l
tot Al	...	...	...	...	...	...	...	...	...	mg/l
dis Al	7.2	4.4	5.3	5.3	5.03	5.027	10.019	8.617	...	mg/l
tot Fe	...	...	...	...	...	...	...	...	...	mg/l
dis Fe	<.05	<.05	<.05	<.05	<.05	.08	.01	<.01	...	mg/l
tot As	...	...	...	.36	...	...	...	...	...	mg/l
tot V	...	...	...	.6	...	...	...	...	...	mg/l
tot alk	...	...	...	...	...	...	...	...	...	mg/l CaCO3
dis alk	665	700	510	505	525	550	550	505	...	mg/l CaCO3
Cl	38	37	37	37	35	35	35	36	...	mg/l
SO4	45.6	42	39.6	39.6	44.4	43	39.6	32.6	...	mg/l as S
dis SiO2	.97	1.16	1.91	1.95	.69	.65	1.44	1.86	...	mg/l as Si
B	.125	.125	.125	.15	.05	.1	.1	.1	...	mg/l
NO2	.21	.24	.28	.27	.22	.24	.19	.29	...	mg/l as N
NO3	.8	2	2.4	2.3	2.6	2.3	3.4	3.95	...	mg/l as N
NH3	.4	.2	.4	.4	.4	.55	.03	.03	...	mg/l as N
F	1.8	1.7	2	1.8	1.7	2.8	3	2.1	...	mg/l
PO4	.06	.06	.04	.03	.04	.07	.07	.12	...	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	% as O
EC	1010	1020	1090	1100	1060	1050	1000	1060	...	mhos/cm
SS	39	26	25	32	68	78	26	32	...	mg/l
ash	...	...	...	...	...	...	...	...	...	mg/l
chl'phyll	58	<10	<10	21	...	33	131	56	...	ug/l

KINGHORN LOCH AT OUTLET for 1/2/83 to 16/3/83

date	1/2/83	9/2/83	15/2/83	20/2/83	26/2/83	28/2/83	1/3/83	7/3/83	16/3/83	
time	1835	0715	1620	1145	1240	1250	1015	1610	0910	
flow	...	13	18	5	5	5	<5	9	13	l/s
temp	2	0	2	2	2	2.5	2	5.5	6	C
pH	9.9	9.9	9.8	9.8	10	10.1	10	10.2	10.1	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	6.1	3.6	1.9	3.4	6.1	...	3.6	2.8	2.4	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	1.15	1.8	.7	1.1	8.1	...	1.4	1.1	.8	mg/l
Na	262	267	261	171	255	...	256	272	285	mg/l
K	3.54	3.36	3.58	3.51	3.64	...	3.58	3.9	3.31	mg/l
tot Al	...	...	...	...	...	10.8	...	...	...	mg/l
dis Al	9.188	5.027	4.428	4.81	9.57	...	4.8	5.03	5.59	mg/l
tot Fe	...	...	...	...	...	...	...	...	...	mg/l
dis Fe	<.01	<.01	<.01	.04	.01	...	.03	.08	.02	mg/l
tot As	.31	...	...	...	...	.14	...	...	...	mg/l
tot V	.6	...	...	...	...	.1	...	...	...	mg/l
tot alk	...	...	...	...	...	510	...	...	...	mg/l CaCO3
dis alk	505	485	490	480	525	440	485	490	495	mg/l CaCO3
Cl	36	34	38	38	64	...	33	40	33	mg/l
SO4	34	37	33.3	35.6	32.6	...	35.6	43.3	46.3	mg/l as S
dis SiO2	1.39	.93	1.77	1.16	1.95	...	2.09	.69	.88	mg/l as Si
B	.1	.15	.15	.15	.2	...	.2	.15	.15	mg/l
NO2	.32	.37	.38	.39	.24	...	.44	.89	.47	mg/l as N
NO3	3.9	3.7	4	3.9	1.2	...	3.6	4	3.2	mg/l as N
NH3	<.01	.2	.01	.7	.6	...	.4	.01	.02	mg/l as N
F	1.7	1.6	1.65	1.75	1.7	...	1.7	1.75	1.75	mg/l
PO4	.08	.13	.22	.06	.05	...	.05	.07	.05	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	% as O
EC	1075	1060	1050	1090	1020	890	1060	1020	1050	mhos/cm
SS	21	43	60	53	19	16	54	61	61	mg/l
ash	...	...	...	...	...	...	...	...	...	mg/l
chl'phyll	21	32	...	66	...	133	10	...	23	ug/l

KINGHORN LOCH AT OUTLET for 27/3/83 to 15/5/83

date	27/3/83	1/4/83	14/4/83	18/4/83	22/4/83	26/4/83	1/5/83	12/5/83	15/5/83	
time	2010	1016	1805	1240	0715	1045	1640	1750	1300	
flow	51	22	5	5	5	5	26	29	39	l/s
temp	4	5	7	7	7	7.5	8	9	9	C
pH	9.9	10.1	10.1	9.9	10	10	9.8	10	10	
tot Ca	...	...	...	...	...	...	...	...	...	mg/l
dis Ca	3	...	2.7	3.9	2.5	2.7	2.7	1.1	1.8	mg/l
tot Mg	...	...	...	...	...	...	...	...	...	mg/l
dis Mg	.8	...	4.1	7.5	2.7	5.3	7.3	<.1	<.1	mg/l
Na	242	...	247.2	250.5	259.1	222.3	252.9	240	209	mg/l
K	3.54	...	3	3.3	3.64	2.81	3.27	3.3	3.35	mg/l
tot Al	...	...	...	...	...	10.2	...	...	...	mg/l
dis Al	4.7	...	4.4	6.4	5	7.7	4.1	3.2	3.6	mg/l
tot Fe	...	...	...	...	...	...	...	...	...	mg/l
dis Fe	<.01	...	.08	.02	.12	.11	.07	<.1	<.1	mg/l
tot As	...	...	.31	...	...	...	...	.34	...	mg/l
tot V	...	...	.6	...	...	...	...	.6	...	mg/l
tot alk	...	...	...	...	...	...	...	...	...	mg/l CaCO3
dis alk	450	460	455	470	480	490	475	475	480	mg/l CaCO3
Cl	37	37	39	39	41	40	39	37	36	mg/l
SO4	41	38.3	44	41.6	43.6	37.3	44	39.6	39.6	mg/l as S
dis SiO2	1.11	1.07	.93	.97	1.21	.83	.88	.69	.69	mg/l as Si
B	.15	.05	.15	.05	.15	.25	.25	.2	.25	mg/l
NO2	.43	.49	.48	.54	.46	.5	.51	.44	.41	mg/l as N
NO3	2	2.7	2	2.45	1.8	2	2.3	1.65	1.4	mg/l as N
NH3	.3	.6	.02	.02	<.1	.02	.01	<.01	.01	mg/l as N
F	...	...	1.85	1.85	1.85	1.6	2.15	2.05	2.15	mg/l
PO4	.06	.07	.1	.05	.2	.09	.12	.05	.05	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	% as O
EC	1080	930	1025	1075	1000	950	1020	1300	1300	mhos/cm
SS	45	51	50	55	50	80	71	55	48	mg/l
ash	...	...	...	...	...	...	...	...	...	mg/l
chl'phyll	42	191	52	165	268	...	229	66	154	ug/l

KINGHORN LOCH AT OUTLET for 24/5/83 to 24/5/83

date	24/5/83	
time	1110	
flow	<5	l/s
temp	12	C
pH	10.3	
tot Ca	...	mg/l
dis Ca	1	mg/l
tot Mg	...	mg/l
dis Mg	.7	mg/l
Na	264	mg/l
K	2.85	mg/l
tot Al	...	mg/l
dis Al	3.5	mg/l
tot Fe	...	mg/l
dis Fe	<.01	mg/l
tot As	...	mg/l
tot V	...	mg/l
tot alk	...	mg/l CaCO3
dis alk	475	mg/l CaCO3
Cl	37	mg/l
SO4	37.6	mg/l as S
dis SiO2	1.72	mg/l as Si
B	.2	mg/l
NO2	.01	mg/l as N
NO3	<.1	mg/l as N
NH3	.5	mg/l as N
F	2.05	mg/l
PO4	.21	mg/l as P
BOD	...	mg/l as O
DO	...	mg/l as O
DO	...	% as O
EC	1060	mhos/cm
SS	57	mg/l
ash	...	mg/l
chl'phyll	62	ug/l

KINGHORN LOCH AT OUTLET
statistical appraisal - for 4/1/81 to 24/5/83

	samples	maximum	minimum	mean	std.dev.	n20	n10	n5	
flow	112	80	<5	20.8259	19.8216	87	348	1392	l/s
temp	118	21	0	8.7072	5.64846	40	162	647	C
pH	125	10.5	9.2	9.9432	.26635	27	109	681	
tot Ca	53	56.8	.3	11.1396	12.5653	122	489	1955	mg/l
dis Ca	106	15.7	.2	3.40188	2.50975	52	209	836	mg/l
tot Mg	53	22.4	2.6	10.4396	5.26664	24	98	391	mg/l
dis Mg	106	19	<.1	4.34632	3.94903	79	317	1269	mg/l
Na	117	335	151	251.806	33.9666	2	7	28	mg/l
K	117	6	2	3.64505	.665844	3	13	51	mg/l
tot Al	63	12.7	3.3	7.33968	2.04887	7	30	120	mg/l
dis Al	111	16.1	1.7	6.61024	2.31999	12	47	189	mg/l
tot Fe	44	.8	<.05	.134318	.155015	128	512	2047	mg/l
dis Fe	75	.42	<.01	.064533	.073347	124	496	1985	mg/l
tot As	32	.45	.14	.32125	.061525	4	14	56	mg/l
tot V	32	.7	.1	.49375	.150133	9	36	142	mg/l
tot alk	65	635	295	426.769	73.1567	3	11	45	mg/l CaCO3
dis alk	122	700	295	471.516	87.2735	3	13	53	mg/l CaCO3
Cl	117	72	23	37.8376	6.14752	3	10	41	mg/l
SO4	115	61.3	20.2	44.2141	7.22565	3	10	41	mg/l as S
dis SiO2	117	2.65	.27	1.19231	.440823	13	53	210	mg/l as Si
B	117	.95	.025	.126538	.104364	65	261	1045	mg/l
NO2	119	.89	<.01	.148109	.163619	117	469	1875	mg/l as N
NO3	119	8.8	.05	1.83575	1.89915	103	411	1645	mg/l as N
NH3	119	1.6	<.01	.264201	.277666	106	424	1697	mg/l as N
F	116	4.8	.17	1.47569	.687441	21	83	333	mg/l
PO4	117	2.4	<.01	.131453	.230456	295	1181	4723	mg/l as P
BOD	2	2.2	.5	1.35	...	...	...	...	mg/l as O
DO	6	12.1	7.6	10.3	1.56587	2	9	36	mg/l as O
DO	6	121.6	80.3	97.3667	14.1671	2	8	33	% as O
EC	124	1550	660	982.016	177.163	3	13	50	mhos/cm
SS	125	88	3	31.104	20.7725	43	171	685	mg/l
ash	2	7	4	5.5	...	...	...	...	mg/l
chl'phyll	80	320	<10	70.375	75.9464	112	447	1790	ug/l

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TABLE A.6. Chemical analysis of Kinghorn Loch at outlet sluice for the period 30-5-1983 to 27-9-1984; without statistical appraisal.

KINGHORN LOCH AT OUTLET for 30/5/83 to 10/7/83

date	30/5/83	31/5/83	5/6/83	14/6/83	22/6/83	28/6/83	1/7/83	8/7/83	10/7/83	
time	1810	1210	1655	1800	1905	1640	0855	0735	0900	
flow	22	5	56	56	5	<5	13	13	16	l/s
temp	12	...	11.5	13	19.5	14	14.5	17.5	17.5	C
pH	10.2	10.1	10.2	10	10.3	10.3	10.2	10.2	10.3	
dis Ca	1.9	...	1.9	2.3	2	1.5	2.4	2.3	1.9	mg/l
dis Mg	2.8	...	.7	1.7	1.2	2.4	4.7	2.6	.7	mg/l
Na	277	...	236	213.9	223	223	224	206.4	202.9	mg/l
K	3.04	...	2.69	2.72	2.76	2.74	2.77	2.7	2.8	mg/l
tot Al	...	6.1	...	...	...	...	...	...	...	mg/l
dis Al	4.3	...	3.6	2.6	2.5	2.2	2.6	2.9	1.6	mg/l
dis Fe	<.01	...	<.1	.06	<.01	<.01	.08	.08	.09	mg/l
tot As	...	.26	...	...	...	...	...	...	...	mg/l
tot V	...	.5	...	...	...	...	...	...	...	mg/l
tot alk	...	470	...	...	...	...	...	...	...	mg/l CaCO3
dis alk	465	470	470	445	425	425	395	390	390	mg/l CaCO3
Cl	37	...	36	38	44	38	34	36	32	mg/l
SO4	35.6	...	28.6	27.3	24	54.3	24.6	60	36	mg/l as S
dis SiO2	.69	...	.93	1.07	1.11	1.11	1.04	1.11	1.58	mg/l as Si
B	.2	...	.2	.15	.1	.15	.1	.15	.2	mg/l
NO2	.35	...	.17	.26	<.01	.02	.09	.1	.01	mg/l as N
NO3	1.2	.9	.5	1	.8	<.1	.1	2.7	<.1	mg/l as N
NH3	1	...	.2	1.4	<.1	.9	1.1	.1	.8	mg/l as N
F	2.05	...	1.95	1.9	1.8	1.8	1.8	1.75	1.75	mg/l
PO4	.04	...	.07	.05	.04	.03	.04	.05	<.01	mg/l as P
BOD	23.1	...	21	28	...	...	...	...	...	mg/l as O
COD	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	% as O
EC	980	1000	1000	970	900	940	940	980	1060	mhos/cm
SS	42	40	53	41	61	51	46	44	59	mg/l
chl'phyll	62	...	206	312.4	291.6	...	...	274.9	76.3	ug/l

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KINGHORN LOCH AT OUTLET for 18/7/83 to 20/9/83

date	18/7/83	26/7/83	1/8/83	6/8/83	8/8/83	20/8/83	1/9/83	12/9/83	20/9/83	
time	0820	0820	1600	1735	1030	2035	1105	0920	0740	
flow	24	29	37	<5	...	<5	<5	<5	<5	l/s
temp	...	18.5	17.5	19.5	...	18.5	17	11.5	9	C
pH	10	9.9	9.5	9.3	9.2	9.7	9.6	9.5	9.6	
dis Ca	1.3	3.2	4.2	.3	...	.5	.4	2.9	3.4	mg/l
dis Mg	1.4	2.5	3	2	...	2.3	2.3	2.8	2.8	mg/l
Na	201.4	222	219	207.9	...	213.6	206.1	217	209.9	mg/l
K	.5	3.7	3.5	3.3	...	3.3	3.2	2.52	2.62	mg/l
tot Al	...	...	...	...	2.1	...	...	...	...	mg/l
dis Al	1.8	...	...	1.2	1.3	1.2	.9	.9	1.2	mg/l
dis Fe	<.05	<.05	<.05	<.05	...	<.05	.05	<.05	<.05	mg/l
tot As	...	...	...	...	.19	...	...	...	...	mg/l
tot V	...	...	...	...	.4	...	...	...	...	mg/l
tot alk	...	...	...	...	375	...	...	...	...	mg/l CaCO3
dis alk	385	390	360	395	375	400	385	395	385	mg/l CaCO3
Cl	36	40	36	36	...	38	33	40	35	mg/l
SO4	41.3	41.3	43	43	...	49	31.6	30	28.6	mg/l as S
dis SiO2	1.67	1.53	1.63	1.77	...	1.44	1.49	1.3	1.39	mg/l as Si
B	.15	.45	.65	.5	...	...	...	.2	.25	mg/l
NO2	.06	.05	.09	.07	...	.08	.08	.01	.27	mg/l as N
NO3	.2	.2	.1	.1	...	.3	.2	1.9	.5	mg/l as N
NH3	.2	.5	1.4	.9	...	.8	.4	1.1	.2	mg/l as N
F	.54	3.3	2.65	2.1	...	1.9	2.2	1.5	1.5	mg/l
PO4	.05	.1	.1	.05	...	.09	.08	.05	.04	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
COD	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	4.5	...	...	...	8.8	...	7	9.7	mg/l as O
DO	...	48.1	...	...	...	94	...	64.3	84	% as O
EC	970	930	920	760	750	940	840	880	910	mhos/cm
SS	34	4	9	15	4	8	12	2	9	mg/l
chl'phyll	225.5	201.1	31	242	...	84.1	36.7	31	38.9	ug/l

KINGHORN LOCH AT OUTLET for 24/9/83 to 9/11/83

date	24/9/83	28/9/83	1/10/83	9/10/83	20/10/83	25/10/83	2/11/83	7/11/83	9/11/83	
time	0715	1120	0930	1650	0845	1810	0835	1725	1030	
flow	<5	...	46	55	<5	<5	<5	14	<5	l/s
temp	11	...	12	...	6.5	8	7.5	10	...	C
pH	9.6	9.6	9.4	9.5	9.3	9	9	9	9	
dis Ca	4.6	3.1	3.6	3.7	5.7	6.5	6.9	7.4	8.6	mg/l
dis Mg	2.8	2	3.1	3.3	5.2	5.1	5.8	5.6	6.5	mg/l
Na	218	196	189	198.5	197.4	184.4	200.1	187.3	184	mg/l
K	3	2.5	3.24	3.13	3.21	3.02	3.23	3.1	2.93	mg/l
tot Al	...	1.9	...	...	...	...	...	...	.9	mg/l
dis Al	1.2	1.6	1.4	1.4	1.1	1.3	1.2	1.1	.9	mg/l
dis Fe	.06	.02	.05	<.01	<.01	<.01	<.01	.05	<.01	mg/l
tot As	...	.29	...	...	...	...	...	...	.19	mg/l
tot V	...	.4	...	...	...	...	...	...	.3	mg/l
tot alk	...	380	...	...	...	...	...	...	350	mg/l CaCO3
dis alk	330	365	395	390	370	360	365	375	350	mg/l CaCO3
Cl	32	37	34	33	34	35	61	34	34	mg/l
SO4	27.3	...	33.3	33.3	31	31	31	32.3	32.3	mg/l as S
dis SiO2	1.58	1.3	1.21	1.11	1.16	1.21	1.11	1.11	1.21	mg/l as Si
B	.18	.18	.2	.15	.1	.1	.1	.1	.1	mg/l
NO2	.28	.26	.32	.15	.11	.22	.075	.3	.16	mg/l as N
NO3	.5	.7	.7	.8	1.6	2	1.9	2.5	2.2	mg/l as N
NH3	.3	.12	.8	.3	.3	.02	.05	.05	.4	mg/l as N
F	.98	...	2	2	1.7	1.2	1.2	1.2	1.4	mg/l
PO4	.04	.06	.07	.03	.13	.11	.09	.12	.05	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
COD	...	...	...	...	...	...	...	...	...	mg/l as O
DO	10.3	...	8.3	...	...	...	...	...	...	mg/l as O
DO	93.5	...	77.1	...	...	...	...	...	...	% as O
EC	910	920	840	830	680	780	740	760	780	mhos/cm
SS	6	14	12	8	6	9	9	2	3	mg/l
chl'phyll	83.3	71	21	<10	<10	...	...	<10	...	ug/l

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KINGHORN LOCH AT OUTLET for 19/11/83 to 17/1/84

date	19/11/83	23/11/83	27/11/83	1/12/83	12/12/83	24/12/83	28/12/83	1/1/84	17/1/84	
time	0815	0725	1510	1640	1430	0...	1440	1315	1045	
flow	<5	<5	<5	<5	<5	...	59	<5	<5	l/s
temp	4	2.5	5	5.5	2.5	...	7	5.5	2	C
pH	8.9	8.9	8.8	8.8	8.7	8.4	8.4	8.4	8.4	
dis Ca	8.8	10.5	10	10.5	9.4	15.2	14.8	15.3	16.5	mg/l
dis Mg	8	7.6	8.3	8.1	8.1	11.6	11.5	10.8	12.5	mg/l
Na	187.1	181.8	178.3	173.2	172.6	151.2	119.8	153.2	135.3	mg/l
K	3.11	3.23	3.11	3.1	2.55	2.54	3.14	2.79	2.59	mg/l
tot Al	...	...	...	...	...	...	...	...	...	mg/l
dis Al	.6	.5	.4	.6	.4	.3	.5	.3	.4	mg/l
dis Fe	<.01	<.01	<.01	<.01	.05	.05	.04	.15	.08	mg/l
tot As	...	...	...	...	...	...	...	...	...	mg/l
tot V	...	...	...	...	...	...	...	...	...	mg/l
tot alk	...	...	...	...	...	...	...	...	...	mg/l CaCO3
dis alk	340	345	340	330	345	305	310	325	245	mg/l CaCO3
Cl	36	36	...	...	...	53	37	36	37	mg/l
SO4	26.6	24	32	22.6	32	28.3	27.6	28.3	28.3	mg/l as S
dis SiO2	1.16	1.16	1.11	1.25	1.16	1.39	1.39	1.35	1.63	mg/l as Si
B	.15	.15	.1	.1	.1	.175	.1	.1	.075	mg/l
NO2	.02	.02	...	...	...	.27	.27	<.01	.34	mg/l as N
NO3	2.4	2.4	2.5	2.5	1.8	3.3	3.3	3.6	5	mg/l as N
NH3	.03	.06	<.1	<.1	.1	.9	<.1	.1	<.1	mg/l as N
F	...	...	...	...	...	...	...	1.1	.96	mg/l
PO4	.08	.08	...	...	...	.13	.07	.02	.02	mg/l as P
BOD	...	...	...	...	...	...	...	...	...	mg/l as O
COD	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	% as O
EC	740	760	680	700	740	550	670	690	660	mhos/cm
SS	12	10	8	3	9	13	13	13	5	mg/l
chl'phyll	<10	...	...	...	<10	...	...	<10	...	ug/l

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KINGHORN LOCH AT OUTLET for 29/1/84 to 21/3/84

date	29/1/84	1/2/84	6/2/84	20/2/84	22/2/84	29/2/84	6/3/84	11/3/84	21/3/84	
time	1540	1005	1305	0745	1525	1040	1000	1735	1000	
flow	>60	...	...	...	...	...	...	...	>50	l/s
temp	2	2	2.5	4	3.5	3	6	6	5.5	C
pH	8.3	8.3	8.3	8.3	8.2	8.4	8.4	8.6	8.5	
dis Ca	20.4	21.6	24.5	27.2	32	31.3	21.2	24.4	23.1	mg/l
dis Mg	13.3	14.2	12.4	14.85	14.59	15.22	16.12	16.3	27.79	mg/l
Na	117.2	116	116.4	99.7	102.5	97.1	101.2	100.7	104.6	mg/l
K	2.36	2.3	2.23	2.14	2.26	2.24	1.99	1.89	3.39	mg/l
tot Al	...	...	...	...	...	.2	...	...	...	mg/l
dis Al	.2	.1	1.7	.44	.1	.1	.8	.9	.6	mg/l
dis Fe	.04	.04	.25	.14	.04	.09	<.01	.06	.05	mg/l
tot As	...	...	...	...	...	...	...	...	...	mg/l
tot V	...	...	...	...	...	...	...	...	...	mg/l
tot alk	...	...	...	...	...	...	...	...	...	mg/l
dis alk	260	270	250	225	265	250	205	245	230	mg/l CaCO3
Cl	38	36	37	33	32	32	41	39	39	mg/l CaCO3
SO4	24.6	30	24	26	26.6	26	25	23.6	23.6	mg/l
dis SiO2	2	2.05	1.81	2.23	2.05	1.86	2.09	2.14	1.95	mg/l as S
B	.075	.075	.075	.1	.075	.1	.1	.05	.1	mg/l as Si
NO2	.025	.02	.02	.02	.02	.02	.47	.37	.03	mg/l
NO3	4.7	5.05	4.8	5.9	6.1	5.9	5.7	5.6	5.25	mg/l as N
NH3	.11	.53	.2	.1	<.1	<.1	.04	.08	.04	mg/l as N
F	.84	.82	.84	.66	.78	.72	.6	.64	.54	mg/l as N
PO4	.05	.07	.04	.01	.02	.02	.03	.02	.02	mg/l
BOD	...	...	...	...	...	...	...	...	...	mg/l as P
COD	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	...	...	...	...	...	...	mg/l as O
EC	640	635	490	620	600	580	580	570	600	% as O
SS	9	1	11	2	2	4	6	8	14	mhos/cm
chl'phyll	<10	...	...	...	<10	...	...	...	<10	mg/l
										ug/l

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KINGHORN LOCH AT OUTLET for 28/3/84 to 25/6/84

date	28/3/84	16/4/84	20/4/84	1/5/84	6/5/84	16/5/84	1/6/84	4/6/84	25/6/84	
time	1105	1915	1610	1715	1810	1215	1850	2010	2030	
flow	...	...	...	...	...	...	...	...	...	l/s
temp	5.5	8	12	13	12	13	14	14	22	C
pH	8.4	8.5	8.5	8.5	8.4	8.5	8.4	8.4	8.3	
dis Ca	23.9	22.6	20.1	23.8	21.9	21.3	26.8	26.8	20.1	mg/l
dis Mg	17.28	17.1	17.9	18.5	18.3	19	18.7	19.2	21.4	mg/l
Na	98.8	100.2	90.9	89.9	94.5	93.8	93.1	93.7	99.9	mg/l
K	1.94	1.93	1.91	1.96	1.68	1.7	1.45	1.22	2.38	mg/l
tot Al	...	...	...	...	...	...	...	...	...	mg/l
dis Al	.8	.4	.4	.8	.6	...	...	...	...	mg/l
dis Fe	.05	...	...	...	...	...	...	...	...	mg/l
tot As	...	...	.056	...	...	...	...	...	...	mg/l
tot V	...	...	<.1	...	...	...	...	...	...	mg/l
tot alk	...	...	...	...	...	...	...	...	...	mg/l
dis alk	220	215	205	210	215	215	240	225	260	mg/l CaCO3
Cl	41	34	35	38	34	36	34	34	33	mg/l CaCO3
SO4	24.3	24.6	26.3	...	...	27	24	23	25.3	mg/l
dis SiO2	2.05	1.95	1.67	1.77	1.58	1.35	1.07	1.07	.18	mg/l as S
B	.05	.1	...	.1	.075	.125	.05	.075	.08	mg/l as Si
NO2	.03	.02	.02	.04	.05	.075	.07	.07	.06	mg/l
NO3	5.3	5.3	5.3	5.4	4.8	4.9	3.4	3.5	2.8	mg/l as N
NH3	.01	<.1	<.1	.3	.2	.12	.4	.3	.1	mg/l as N
F	.58	.5	.52	.54	.52	...	.52	.52	.75	mg/l as N
PO4	.02	.01	.04	...	<.01	.01	<.01	<.01	.03	mg/l
BOD	...	...	...	...	...	...	...	...	...	mg/l as P
COD	...	...	...	...	...	...	...	...	...	mg/l as O
DO	...	...	...	10.4	9.6	...	...	...	...	mg/l as O
DO	...	...	...	98.8	89.2	...	...	...	...	mg/l as O
EC	580	580	580	540	600	580	530	540	580	% as O
SS	7	6	20	3	5	10	14	14	76	mhos/cm
chl'phyll	<10	<10	<10	<10	<10	<10	<10	<10	<10	mg/l
										ug/l

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KINGHORN LOCH AT OUTLET for 5/7/84 to 27/9/84

date	5/7/84	27/9/84		
time	1530	0855		
flow	...	...	l/s	
temp	22	12	C	
pH	8.5	8.7		
dis Ca	...	13.5	mg/l	
dis Mg	...	22.7	mg/l	
Na	102.5	104.1	mg/l	
K	3.4	3	mg/l	
tot Al	...	...	mg/l	
dis Al	...	...	mg/l	
dis Fe	...	<.05	mg/l	
tot As	...	...	mg/l	
tot V	...	...	mg/l	
tot alk	...	...	mg/l	CaCO3
dis alk	220	225	mg/l	CaCO3
Cl	36	37	mg/l	
SO4	25.3	28	mg/l	as S
dis SiO2	.46	.74	mg/l	as Si
B	.15	.07	mg/l	
NO2	.05	.01	mg/l	as N
NO3	2	.15	mg/l	as N
NH3	<.1	.02	mg/l	as N
F	.65	.47	mg/l	
PO4	<.01	.01	mg/l	as P
BOD	...	...	mg/l	as O
COD	...	6	mg/l	as O
DO	...	...	mg/l	as O
DO	...	...	%	as O
EC	620	540	mhos/cm	
SS	8	1	mg/l	
chl'phyll	<10	...	ug/l	

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TABLE A.7. Chemical analysis of Kinghorn Loch over a three dimensional grid of selected sampling stations for 23-2-1981; with statistical appraisal.

KINGHORN LOCH - WATER BODY STATIONS for 23/2/81

station	51(.3m)	50(1m)	48(1m)	46(3.5m)	46(1m)	44(1m)	41(.5m)	39(1m)	37(3.5m)	
temp	1	2	2	2	2	2	1.5	2	2	C
pH	9	9.6	9.6	9.6	9.6	9.6	9.4	9.9	9.6	
dis Ca	14.7	1.9	1.9	1.9	1.9	1.9	3.5	1	2	mg/l
dis Mg	20.5	13.5	13.6	13.6	13.6	14.2	16.9	2.6	13.7	mg/l
Na	133	213	217	215	213	208	186	265	209	mg/l
dis Al	.6	5.8	5.6	7.2	8.4	7.4	3.9	5.3	8	mg/l
dis Fe	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	mg/l
dis alk	220	390	395	390	395	380	330	435	390	mg/l CaCO3
SO4	31.6	42	43	43	42.3	43.3	46	47.3	42.6	mg/l as S
F	.65	1	1	.95	...	1	.95	1.55	...	mg/l
EC	550	825	830	830	825	820	860	975	840	mhos/cm
SS	8	14	11	29	11	11	17	767	11	mg/l

KINGHORN LOCH - WATER BODY STATIONS for 23/2/81

station	37(1m)	35(5m)	35(1m)	33(3m)	33(1m)	31(9m)	31(5m)	31(1m)	29(5m)	
temp	1.5	2	2	2	2	2	2	2	1.5	C
pH	9.6	9.6	9.6	9.6	9.6	9.6	9.6	9.6	9.6	
dis Ca	1.9	1.9	1.8	1.9	1.9	1.9	1.9	1.9	1.9	mg/l
dis Mg	13.6	13.5	13.4	14.3	14.4	14.5	14.6	14.8	14.1	mg/l
Na	212	213	212	213	216	213	211	219	217	mg/l
dis Al	5.6	6.5	8.2	7.9	5.8	8.5	7.3	9.6	5.8	mg/l
dis Fe	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	mg/l
dis alk	390	395	395	390	395	390	395	390	385	mg/l CaCO3
SO4	44.3	43.6	44.3	45	44.3	44.3	44.3	43.3	42	mg/l as S
F	1.1	1.1	...	...	1.2	...	1.2	...	1.25	mg/l
EC	840	840	840	845	840	840	840	840	840	mhos/cm
SS	10	12	12	12	12	12	11	11	12	mg/l

KINGHORN LOCH - WATER BODY STATIONS for 23/2/81

station	29(1m)	27(3m)	27(1m)	25(1m)	23(6.5m)	23(1m)	21(10m)	21(9m)	21(5m)	
temp	1.5	2	1.5	1.5	2	2	2	2	2	C
pH	9.6	9.6	9.6	9.6	9.6	9.6	9.6	9.6	9.6	
dis Ca	1.9	1.8	1.8	1.8	1.8	2	2	1.9	2	mg/l
dis Mg	14	14.5	14.8	14.2	13.8	13.7	14.4	13.9	14.5	mg/l
Na	214	220	220	216	218	221	224	225	226	mg/l
dis Al	7.7	7.8	6.5	6.4	7	5.2	7.5	8.5	8.1	mg/l
dis Fe	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	mg/l
dis alk	395	395	390	390	395	390	390	390	395	mg/l CaCO3
SO4	41.6	43.6	43.6	43.3	44.6	43.6	43	43.6	43.6	mg/l as S
F	...	...	1.25	1.35	...	1.3	...	...	1.3	mg/l
EC	840	830	825	820	835	840	840	840	835	mhos/cm
SS	11	16	12	12	13	12	12	10	11	mg/l

KINGHORN LOCH - WATER BODY STATIONS for 23/2/81

station	21(1m)	19(4.5m)	19(1m)	17(1m)	15(9m)	15(5m)	15(1m)	13(9m)	13(5m)	
temp	2	2	2	2	2	2	2	2	2	C
pH	9.6	9.6	9.6	9.6	9.6	9.6	9.6	9.6	9.6	
dis Ca	1.9	1.9	1.9	1.9	1.8	2	1.8	1.9	2	mg/l
dis Mg	14.4	13.8	14	14.2	13.6	14.5	14.1	13.9	14.1	mg/l
Na	225	226	227	228	222	223	218	219	222	mg/l
dis Al	9.4	9.6	6.6	5.5	7.3	5.4	7.6	7.1	5.2	mg/l
dis Fe	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	mg/l
dis alk	390	385	385	380	390	390	390	390	385	mg/l CaCO3
SO4	42.3	40.3	42.6	44.3	43.6	44	44	43.6	43	mg/l as S
F	...	...	1.3	1.25	...	1.25	...	...	1.55	mg/l
EC	830	840	840	840	835	835	835	840	840	mhos/cm
SS	11	12	11	13	10	13	12	62	12	mg/l

KINGHORN LOCH - WATER BODY STATIONS for 23/2/81

station	13(1m)	11(2.5m)	11(1m)	9(4m)	9(1m)	7(6.5m)	7(5m)	7(1m)	5(4.5m)	
temp	2	2	2	2	2	2	2	2	2	C
pH	9.6	9.6	9.6	9.6	9.6	9.6	9.6	9.6	9.6	
dis Ca	1.9	2	1.9	1.8	3.3	2	1.9	1.9	2	mg/l
dis Mg	14.2	14	13.7	13.7	14.3	14	13.9	13.9	13.8	mg/l
Na	221	217	218	218	227	228	225	229	226	mg/l
dis Al	7.4	5.3	7.1	7.1	4.3	5.5	4.9	7.8	8.1	mg/l
dis Fe	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	mg/l
dis alk	390	395	390	375	385	385	390	385	380	mg/l CaCO3
SO4	43.6	42.3	41.3	44	44	45	45	43.6	42.3	mg/l as S
F	...	1.7	...	...	1.3	...	1.6	...	...	mg/l
EC	840	830	830	835	830	835	835	840	820	mhos/cm
SS	12	12	11	10	12	10	12	10	16	mg/l

KINGHORN LOCH - WATER BODY STATIONS for 23/2/81

station	5(1m)	3(1m)	1(1m)	
temp	2	2	1.5	C
pH	9.6	9.6	9.6	
dis Ca	1.9	1.4	2.1	mg/l
dis Mg	14.1	14	14.6	mg/l
Na	220	219	225	mg/l
dis Al	4.9	6.5	4.8	mg/l
dis Fe	<.1	<.1	<.1	mg/l
dis alk	375	385	380	mg/l CaCO3
SO4	43.6	42	43	mg/l as S
F	1.6	1.4	1.3	mg/l
EC	820	820	810	mhos/cm
SS	11	221	15	mg/l

KINGHORN LOCH - WATER BODY STATIONS
statistical appraisal - for 23/2/81

	samples	maximum	minimum	mean	std.dev.	n20	n10	n5	
temp	48	2	1	1.90625	.222563	1	5	21	C
pH	48	9.9	9	9.58963	.09648	4	14	89	
dis Ca	48	14.7	1	2.20625	1.87441	69	277	1109	mg/l
dis Mg	48	20.5	2.6	14	1.9929	2	8	31	mg/l
Na	48	265	133	217.75	15.922	1	2	8	mg/l
dis Al	48	9.6	.6	6.65625	1.65694	6	24	95	mg/l
dis Fe	48	<.1	<.1	.05	0	0	0	0	mg/l
dis alk	48	435	220	385	27.1521	0	2	8	mg/l CaCO3
SO4	48	47.3	31.6	43.2167	2.09038	0	1	4	mg/l as S
F	26	1.7	.65	1.24615	.240796	4	14	57	mg/l
EC	48	975	550	831.354	46.964	0	1	5	mhos/cm
SS	48	767	8	33.3333	112.493	1094	4375	17501	mg/l

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TABLE A.8. Chemical analysis of Kinghorn Loch over a three dimensional grid of selected sampling stations for 1-7-1981; with statistical appraisal.

KINGHORN LOCH — WATER BODY STATIONS for 1/7/81

station	50(.8m)	48(.8m)	46(3m)	46(1m)	44(.5m)	39(.8m)	37(3m)	37(1m)	35(4.5m)	
temp	16	16	16	16	16	16	16	16	16	C
pH	10	10	10	9.9	9.9	11.1	9.9	10	10	
dis Ca	11.7	10.3	10	12.8	16.9	21.9	15.6	14.6	15.1	mg/l
dis Mg	7.5	7.4	7.8	7.8	8.2	4.9	7.9	7.9	8	mg/l
Na	207	206	210	211	213	634	200	207	211	mg/l
dis Al	5.9	5.2	5	5.6	5.3	24	4.6	5.5	5.2	mg/l
dis Fe	.05	.06	.11	.04	.02	.09	.06	.05	.05	mg/l
dis alk	370	375	360	370	365	1090	370	365	365	mg/l CaCO3
SO4	44.3	47	47	47	47	68	56	47	47	mg/l as S
F	1.6	1.4	1.55	1.55	1.55	.8	1.55	1.35	1.35	mg/l
DO	9.5	9.7	9.3	...	9.6	4.8	9	9.6	9.8	mg/l as O
DO	96.3	98.4	94.3	...	97.3	48.7	91.3	97.3	99.4	% as O
EC	790	790	780	780	740	1870	790	790	800	mhos/cm
SS	18	20	33	12	10	8652	588	14	64	mg/l

KINGHORN LOCH — WATER BODY STATIONS for 1/7/81

station	35(1m)	33(3m)	33(1m)	31(8.5m)	31(5m)	31(1m)	29(4.5m)	29(1m)	27(2.5m)	
temp	16	16	16	14.5	16	16.5	16.5	16.5	16	C
pH	9.9	9.9	9.9	9.9	10	10	10	10	10	
dis Ca	12.8	13.5	13.9	16.7	14.6	13.7	15.7	13.8	12.2	mg/l
dis Mg	7.6	7.6	7.7	8.6	7.3	7.7	8	7.8	7.6	mg/l
Na	213	211	214	241	214	211	204	212	216	mg/l
dis Al	4.8	5.8	6	7.2	5.1	5	5.9	4.9	4.8	mg/l
dis Fe	.06	.04	.02	.03	.02	.18	.17	.15	.17	mg/l
dis alk	365	370	365	470	370	380	375	385	385	mg/l CaCO3
SO4	51.6	47	47	48.6	63.6	47	47	47	47	mg/l as S
F	1.25	1.4	1.1	.75	1.2	1.55	1.25	1.35	1.55	mg/l
DO	9.7	9	9.5	5	9.6	9.8	9.5	9.5	8.6	mg/l as O
DO	98.4	91.3	96.3	49.1	97.3	100.4	97.3	97.3	87.2	% as O
EC	800	800	810	890	790	800	790	780	780	mhos/cm
SS	20	19	24	8	28	16	27	5	15	mg/l

KINGHORN LOCH - WATER BODY STATIONS for 1/7/81

station	27(1m)	25(.8m)	23(6m)	23(5m)	23(1m)	21(8.5m)	21(5m)	21(1m)	19(4m)	
temp	16	16	15.5	16	16	14.5	16	16	16	C
pH	10	9.9	9.9	9.9	9.9	10.1	10	10	9.9	
dis Ca	13.7	13.3	14.9	16.1	14.5	13.6	14.1	12.4	12	mg/l
dis Mg	7.6	7	6.9	7.1	9.5	10.4	9.1	8.6	8.5	mg/l
Na	213	214	193	216	232	317	223	217	217	mg/l
dis Al	4.8	5	5	6.3	3.5	9.2	4.6	3.8	5.8	mg/l
dis Fe	.18	.18	.11	.12	.02	.06	.14	.05	.11	mg/l
dis alk	375	370	360	370	375	625	375	380	365	mg/l CaCO3
SO4	47	47	61	53.6	73	52.6	47	47	47	mg/l as S
F	1.4	1.35	1.35	1.35	1.55	1.05	1.55	1.4	1.25	mg/l
DO	9.4	9.1	9.1	9.1	9.7	2.9	9.8	9.8	9.7	mg/l as O
DO	95.3	92.3	91.3	92.3	98.4	28.5	99.4	99.4	98.4	% as O
EC	780	770	780	780	810	1100	770	770	770	mhos/cm
SS	20	38	16	19	31	16	22	21	32	mg/l

KINGHORN LOCH - WATER BODY STATIONS for 1/7/81

station	19(1m)	17(.8m)	15(8.5m)	15(5m)	15(1m)	13(8.5m)	13(5m)	13(1m)	11(2m)	
temp	16	16	15	16	16	14.5	15.5	16	16	C
pH	9.9	9.9	9.9	9.9	9.9	9.8	9.9	9.9	9.9	
dis Ca	11.4	12.9	10.2	13.6	14.3	13	13.4	14.1	12.6	mg/l
dis Mg	8	7.8	7.6	9.8	8.9	9.8	8.4	8.1	7.7	mg/l
Na	217	219	221	221	218	245	223	225	220	mg/l
dis Al	6.3	6.4	5.7	5.8	4.8	6.6	5.2	3.8	4.8	mg/l
dis Fe	.02	.02	.05	.07	.06	.07	.04	.06	.03	mg/l
dis alk	370	375	370	370	365	420	370	370	365	mg/l CaCO3
SO4	47	47	47	47	51.6	52.6	47	47	47	mg/l as S
F	1.3	1	1.25	1.4	.9	1.4	1.4	1.35	1.3	mg/l
DO	9.7	9.6	9.4	9.4	10.1	4.2	9.2	9.6	8.7	mg/l as O
DO	98.4	97.3	93.3	95.3	102.4	41.2	92.3	97.3	88.2	% as O
EC	780	780	770	770	770	830	780	785	770	mhos/cm
SS	13	16	29	17	15	9	13	12	19	mg/l

KINGHORN LOCH - WATER BODY STATIONS for 1/7/81

station	11(1m)	9(3.5m)	9(1m)	7(6m)	7(5m)	7(1m)	5(4m)	5(1m)	3(1m)	
temp	16	16	16	16	16	16	15.5	16	...	C
pH	9.9	9.9	9.9	9.9	9.9	9.9	9.9	9.9	9.9	
dis Ca	13.8	17.4	9.4	12.3	11.5	11.5	13.7	12.4	10	mg/l
dis Mg	7.6	7.8	8.7	8.7	8.5	7.9	7.8	7.6	7.6	mg/l
Na	219	225	228	228	229	226	223	224	223	mg/l
dis Al	4.7	5.8	5.7	6.2	5.3	4.9	3.9	5.5	4.7	mg/l
dis Fe	.13	.06	.02	.11	.06	.03	.07	.03	.08	mg/l
dis alk	370	375	370	365	365	365	360	375	375	mg/l CaCO3
SO4	47	56	47	52.3	47	62.3	47	47	45	mg/l as S
F	1.25	1.3	1.3	1.25	1.3	1.2	1.3	1.25	1	mg/l
DO	9.3	8.4	9.3	9	9.3	9.5	9.8	9.5	9.8	mg/l as O
DO	94.3	85.2	94.3	91.3	94.3	96.3	98.3	96.3	...	% as O
EC	770	770	770	790	790	780	770	770	730	mhos/cm
SS	25	35	26	79	40	15	158	18	42	mg/l

KINGHORN LOCH - WATER BODY STATIONS for 1/7/81

station	1(1m)	
temp	16	C
pH	9.9	
dis Ca	11.7	mg/l
dis Mg	7.1	mg/l
Na	218	mg/l
dis Al	4.9	mg/l
dis Fe	.07	mg/l
dis alk	360	mg/l CaCO3
SO4	47	mg/l as S
F	1.1	mg/l
DO	9.7	mg/l as O
DO	98.4	% as O
EC	730	mhos/cm
SS	21	mg/l

KINGHORN LOCH - WATER BODY STATIONS
statistical appraisal - for 1/7/81

	samples	maximum	minimum	mean	std.dev.	n20	n10	n5	
temp	45	16.5	14.5	15.8778	.441539	0	0	1	C
pH	46	11.1	9.8	9.95648	.183759	13	52	324	
dis Ca	46	21.9	9.4	13.4696	2.23562	3	11	42	mg/l
dis Mg	46	10.4	4.9	7.98696	.885309	1	5	19	mg/l
Na	46	634	193	228.891	63.5012	7	30	118	mg/l
dis Al	46	24	3.5	5.75652	2.90934	25	98	393	mg/l
dis Fe	46	.18	.02	.074347	.049245	42	169	674	mg/l
dis alk	46	1090	360	394.457	112.542	8	31	125	mg/l CaCO3
SO4	46	73	44.3	50.0457	6.23331	1	6	24	mg/l as S
F	46	1.6	.75	1.30217	.197188	2	9	35	mg/l
DO	45	10.1	2.9	8.96889	1.55691	3	12	46	mg/l as O
DO	44	102.4	28.5	90.6205	16.1923	3	12	49	% as O
EC	46	1870	730	813.152	167.77	4	16	65	mhos/cm
SS	46	8652	5	225.87	1272.9	3050	12201	48803	mg/l

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TABLE A.9. Chemical analysis of Kinghorn Loch over a three dimensional grid of selected sampling stations for 24-8-1981; with statistical appraisal.

KINGHORN LOCH - WATER BODY STATIONS for 24/8/81

station	50(1m)	48(.5m)	46(1m)	44(.5m)	39(.5m)	37(2.5m)	37(1m)	35(4m)	35(1m)	
temp	17.5	18	17.5	17.5	16.5	17	17.5	16	17	C
pH	9.8	9.8	9.8	9.8	9.9	9.8	9.8	9.7	9.8	
dis Ca	3.9	7	4	3.8	3.6	3.7	3.6	3.8	2.9	mg/l
dis Mg	5.4	6.8	5.4	5.2	5.1	5.2	5.2	5	5.2	mg/l
Na	252	256	253	257	269	247	248	249	251	mg/l
dis Al	5.2	5.1	5.2	4.9	6.3	4.6	5.1	5.1	4.6	mg/l
dis Fe	.08	.22	.09	.07	.09	.08	.08	.09	.07	mg/l
dis alk	405	410	405	410	455	405	405	400	410	mg/l CaCO3
SO4	45.3	45	45.3	45	46.3	45.3	45.3	44.6	44.6	mg/l as S
F	.5	.5	.48	.5	.5	.5	.54	.5	.56	mg/l
sulphide	...	...	...	...	...	...	...	...	...	mg/l as S
DO	12	12.4	12	12.3	11.4	11.8	11.8	8.1	12.3	mg/l as O
DO	125.6	131.1	125.6	128.7	116.8	122.2	123.5	82.1	127.4	% as O
EC	850	850	860	850	910	850	850	840	870	mhos/cm

KINGHORN LOCH - WATER BODY STATIONS for 24/8/81

station	33(2m)	33(1m)	31(9m)	31(5m)	31(1m)	29(4.5m)	29(1m)	27(2m)	27(1m)	
temp	17	17	15.5	16	17	16	17	17	17	C
pH	9.8	9.8	9.7	9.7	9.8	9.7	9.8	9.7	9.8	
dis Ca	3.5	3.8	4.5	4.3	3.8	4.5	4.3	7.2	3.6	mg/l
dis Mg	5.2	5.3	5.5	5.2	5.3	5.3	5	7.2	5.1	mg/l
Na	252	253	243	245	245	250	246	252	249	mg/l
dis Al	5.3	5.2	5.1	5.4	5	5	5.3	6.5	4.8	mg/l
dis Fe	.05	.07	.13	.07	.06	.04	.04	.19	.06	mg/l
dis alk	410	410	410	405	405	405	405	400	405	mg/l CaCO3
SO4	45.6	45	45.3	45	45.3	45.3	48.3	46	46.3	mg/l as S
F	.6	.6	.6	.59	.6	.56	.56	.56	.54	mg/l
sulphide	...	...	.14	...	...	...	...	...	...	mg/l as S
DO	11.9	11.9	6.6	8.5	12	8.3	12.1	10.2	11.8	mg/l as O
DO	123.2	123.2	66.2	86.2	124.3	84.2	125.3	105.6	122.2	% as O
EC	850	850	850	850	850	850	840	850	840	mhos/cm

KINGHORN LOCH - WATER BODY STATIONS for 24/8/81

station	25(.5m)	23(5m)	23(1m)	21(9m)	21(5m)	21(1m)	19(3.5m)	19(1m)	17(1m)	
temp	17.5	16	17	15.5	16	17	16.5	17.5	17.5	C
pH	9.7	9.7	9.8	9.9	9.8	9.8	9.7	9.8	9.7	
dis Ca	5.4	4.3	4.2	293	4.3	4.2	6.1	3.4	39.3	mg/l
dis Mg	5.8	4.9	5	74.5	5.2	5.2	5.8	5.1	18.9	mg/l
Na	252	238	244	300	245	246	245	250	255	mg/l
dis Al	5.5	4.8	5.8	59.5	4.4	5.1	5.4	4.7	12.9	mg/l
dis Fe	.05	.15	.15	19.5	.09	.09	.17	.08	1.19	mg/l
dis alk	410	395	390	615	410	410	400	400	405	mg/l CaCO3
SO4	45.6	46	45.6	48.6	47.6	46	46.6	45.3	47	mg/l as S
F	.48	.5	.5	.84	.48	.5	.44	.44	.46	mg/l
sulphide	...	...	...	2.48	...	...	...	...	...	mg/l as S
DO	11.2	8.7	11.8	<.5	8.1	11.9	11.3	11.9	11.4	mg/l as O
DO	117.2	88.2	122.2	5	82.1	123.2	115.8	124.5	119.3	% as O
EC	840	830	830	1010	850	850	830	860	840	mhos/cm

KINGHORN LOCH - WATER BODY STATIONS for 24/8/81

station	15(8m)	15(5m)	15(1m)	13(8m)	13(5m)	13(1m)	11(2m)	11(1m)	9(3m)	
temp	15.5	16.5	17	15	16	17	17	17	16.5	C
pH	9.7	9.7	9.8	9.9	9.7	9.7	9.7	9.7	9.7	
dis Ca	14.7	4	3.7	4.2	3.9	3.8	4.9	3.8	3.7	mg/l
dis Mg	8.2	5.2	5.2	5.5	5.1	5.2	5.6	5.3	5.1	mg/l
Na	227	233	239	357	239	241	239	244	244	mg/l
dis Al	7.7	4.7	5.3	13.3	4.8	5.2	5.2	5	5.2	mg/l
dis Fe	.81	.08	.08	.24	.05	.06	.17	.1	.02	mg/l
dis alk	405	410	410	760	410	410	410	405	410	mg/l CaCO3
SO4	46.3	46.6	58.6	51.3	55	46.3	47	103.3	46.6	mg/l as S
F	.54	.48	.46	.84	.34	.54	.4	.48	.48	mg/l
sulphide	.06	...	...	>2	...	...	...	...	...	mg/l as S
DO	7.6	8.6	11.6	<.5	8.8	11.9	10.9	11.5	8.6	mg/l as O
DO	76.2	88.1	120.1	5	89.2	123.2	112.9	119.1	88.1	% as O
EC	840	840	860	1130	850	840	840	830	830	mhos/cm

KINGHORN LOCH - WATER BODY STATIONS for 24/8/81

station	9(1m)	7(5m)	7(1m)	5(3.5m)	5(1m)	3(.5m)	1(.5m)	
temp	17	16.5	17	17	17.5	17.5	18	C
pH	9.7	9.7	9.7	9.8	9.8	9.8	9.8	
dis Ca	4.1	3.9	2.6	2.8	2.6	2.1	2.4	mg/l
dis Mg	5.3	5.2	5.1	5.2	5.1	5.2	4.9	mg/l
Na	244	244	247	252	258	256	256	mg/l
dis Al	4.9	5	4.6	4.4	5.1	4.7	4.5	mg/l
dis Fe	<.01	.03	.01	.01	.01	.02	.02	mg/l
dis alk	405	400	410	410	400	410	400	mg/l CaCO3
SO4	46.6	46.3	47.3	45.3	47.3	46.6	46.6	mg/l as S
F	.48	.59	1.45	.7	.84	.6	.59	mg/l
sulphide	...	...	...	...	...	...	...	mg/l as S
DO	12	8.9	11.7	11.9	12.3	12.5	12.6	mg/l as O
DO	124.3	91.2	121.2	123.2	128.7	130.8	133.2	% as O
EC	840	840	840	840	830	820	790	mhos/cm

KINGHORN LOCH - WATER BODY STATIONS
statistical appraisal - for 24/8/81

	samples	maximum	minimum	mean	std.dev.	n20	n10	n5	
temp	43	18	15	16.8023	.699835	0	1	3	C
pH	43	9.9	9.7	9.76278	.06397	2	6	39	
dis Ca	43	293	2.1	11.7953	44.2693	1353	5411	21645	mg/l
dis Mg	43	74.5	4.9	7.31163	10.7078	206	824	3296	mg/l
Na	43	357	227	251.442	19.6983	1	2	9	mg/l
dis Al	43	59.5	4.4	6.77674	8.42428	148	594	2375	mg/l
dis Fe	43	19.5	<.01	.57593	2.96187	2540	10160	40641	mg/l
dis alk	43	760	390	420	62.4685	2	8	34	mg/l CaCO3
SO4	43	103.3	44.6	48.0024	9.01578	3	14	54	mg/l as S
F	43	1.45	.34	.56372	.173111	9	36	145	mg/l
sulphide	4	2.48	.06	1.17	1.2514	110	439	1758	mg/l as S
DO	43	12.6	<.5	10.3628	2.79319	7	28	112	mg/l as O
DO	43	133.2	5	107.335	29.126	7	28	113	% as O
EC	43	1130	790	854.884	52.4305	0	1	6	mhos/cm

TABLE A.10. Chemical analysis of Kinghorn Loch over a three dimensional grid of selected sampling stations for 5-10-1981; with statistical appraisal.

KINGHORN LOCH - WATER BODY STATIONS for 5/10/81

station	45(BOT-.5m)	39(BOT-.5m)	35(BOT-.5m)	30(BOT-.5m)	27(BOT-.5m)	23(BOT-.5m)	21(BOT-.5m)	14(BOT-.5m)	7(BOT-.5m)	
temp	11	11	11	11	11	11	10	11	11	C
pH	9.7	9.8	9.7	9.7	9.7	9.7	9.7	11	9.7	
dis Ca	5	5.3	5	5.2	5.1	5.2	5.1	5.6	4.9	mg/l
dis Mg	5.1	4.6	5.1	6	5.5	5.6	5.5	.8	5.3	mg/l
Na	273	291	282	283	286	283	282	986	271	mg/l
K	2.8	2.9	2.8	2.9	2.8	2.9	2.8	9.3	2.7	mg/l
dis Al	7	8.1	7.6	7.6	8.7	7.2	7.4	65.7	7.1	mg/l
dis Fe	.66	.37	.12	.08	.08	.06	.08	.06	.2	mg/l
dis alk	495	555	495	505	505	505	515	2080	495	mg/l CaCO3
Cl	41	41	38	41	38	44	41	51	44	mg/l
SO4	45	47	54.3	46.6	46.6	47	47.3	73.3	52	mg/l as S
dis SiO2	.97	.97	.83	.97	.79	.93	.97	2.14	.46	mg/l as Si
B	.05	.05	.05	.1	.1	.1	.1	.35	<.05	mg/l
NO2	.01	.01	.01	.03	<.01	.02	.03	.11	.02	mg/l as N
NO3	.4	.1	.35	.35	.05	.35	.3	5	3.5	mg/l as N
NH3	.12	.02	.1	.03	.02	.1	.08	.74	.09	mg/l as N
F	1.6	1.9	1.6	1.6	1.8	1.6	1.7	3.7	1.6	mg/l
PO4	.12	.09	.16	.14	.08	.2	.19	.44	.11	mg/l as P
sulphide	.24	.26	.37	.91	.24	.34	.26	6.4	<.05	mg/l as S
DO	9	9.7	8.8	8.2	9.5	9	8.7	3.6	9.5	mg/l as O
DO	81.7	88	79.9	74.4	86.2	81.7	77.1	32.7	86.2	% as O
EC	930	960	920	930	940	960	910	2770	925	mhos/cm

KINGHORN LOCH - WATER BODY STATIONS for 5/10/81

station	5(BOT-.5m)	
temp	10	C
pH	9.7	
dis Ca	5.2	mg/l
dis Mg	5.4	mg/l
Na	276	mg/l
K	2.7	mg/l
dis Al	7.3	mg/l
dis Fe	.09	mg/l
dis alk	475	mg/l CaCO3
Cl	42	mg/l
SO4	45	mg/l as S
dis SiO2	.79	mg/l as Si
B	.05	mg/l
NO2	.02	mg/l as N
NO3	.1	mg/l as N
NH3	.1	mg/l as N
F	1.6	mg/l
PO4	.1	mg/l as P
sulphide	.21	mg/l as S
DO	9	mg/l as O
DO	79.8	% as O
EC	930	mhos/cm

KINGHORN LOCH - WATER BODY STATIONS
statistical appraisal - for 5/10/81

	samples	maximum	minimum	mean	std.dev.	n20	n10	n5	
temp	10	11	10	10.8	.421649	0	1	2	C
pH	10	11	9.7	9.84	.408945	64	257	1606	
dis Ca	10	5.6	4.9	5.16	.195503	0	1	2	mg/l
dis Mg	10	6	.8	4.89	1.48357	9	35	141	mg/l
Na	10	986	271	351.3	223.091	39	155	620	mg/l
K	10	9.3	2.7	3.46	2.05329	34	135	541	mg/l
dis Al	10	65.7	7	13.37	18.394	182	727	2908	mg/l
dis Fe	10	.66	.06	.18	.19362	111	444	1778	mg/l
dis alk	10	2080	475	662.5	498.482	54	217	870	mg/l CaCO3
Cl	10	51	38	42.1	3.72527	1	3	12	mg/l
SO4	10	73.3	45	50.41	8.57711	3	11	44	mg/l as S
dis SiO2	10	2.14	.46	.982	.436343	19	76	303	mg/l as Si
B	10	.35	<.05	.0975	.093132	88	351	1402	mg/l
NO2	10	.11	<.01	.026499	.030555	128	511	2043	mg/l as N
NO3	10	5	.05	1.14	1.69588	213	850	3401	mg/l as N
NH3	10	.74	.02	.14	.214009	224	898	3591	mg/l as N
F	10	3.7	1.6	1.87	.651576	12	47	187	mg/l
PO4	10	.44	.08	.163	.105519	40	161	644	mg/l as P
sulphide	10	6.4	<.05	.925499	1.93707	421	1683	6731	mg/l as S
DO	10	9.7	3.6	8.5	1.77701	4	17	67	mg/l as O
DO	10	88	32.7	76.77	16.0536	4	17	67	% as O
EC	10	2770	815	1106	586.088	27	108	432	mhos/cm

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TABLE A.11. Chemical analysis of Kinghorn Loch over a three dimensional grid of selected sampling stations for 30-10-1981; with statistical appraisal.

KINGHORN LOCH - WATER BODY STATIONS for 30/10/81

station	50(BOT-.5m)	48(BOT-.5m)	46(BOT-.5m)	46(1m)	44(BOT-.5m)	39(BOT-.5m)	37(BOT-.5m)	37(1m)	35(BOT-.5m)	
temp	7	7	6	6	6	7.5	6	6	6	C
pH	9.9	9.8	9.8	9.8	9.8	10.1	9.9	9.8	9.8	
dis Ca	8.4	5.9	5.5	4.7	5.4	4	4.6	4.7	4.6	mg/l
dis Mg	8.3	7.6	7	6.7	7.1	9.2	7.6	7.6	7.5	mg/l
Na	298	304	312	309	308	399	311	309	307	mg/l
K	4.1	4.3	4.3	4.3	4.3	5.4	4.1	4.2	4.1	mg/l
dis Al	8.1	8.5	8.6	8.6	8.8	11.5	8.7	8.7	8.7	mg/l
dis Fe	<.1	.2	<.1	<.1	<.1	<.1	<.1	<.1	<.1	mg/l
dis alk	525	535	550	555	560	705	565	550	545	mg/l CaCO3
SO4	44	48	48	48	48	54.3	48	48	48	mg/l as S
sulphide	...	...	...	...	...	.55	...	...	.45	mg/l as S
DO	12.5	12.4	12.7	12.6	12.5	12.1	12.3	12.5	12	mg/l as O
DO	103	102.2	102	101.2	100.4	101	98.8	100.4	96.4	% as O
EC	1050	1090	1110	1120	1150	1370	1110	1110	1110	mhos/cm

KINGHORN LOCH - WATER BODY STATIONS for 30/10/81

station	35(1m)	33(BOT-.5m)	33(1m)	31(BOT-.5m)	31(5m)	31(1m)	29(BOT-.5m)	29(1m)	27(BOT-.5m)	
temp	6	6	6	6	6	6	6	6	6	C
pH	9.8	9.8	9.8	9.8	9.8	9.8	9.8	9.9	9.8	
dis Ca	4.6	4.8	5.2	5.3	4.2	4.8	5.7	5.6	5.7	mg/l
dis Mg	7.5	7.7	8	8.1	7.6	8.1	8.3	8.1	8.3	mg/l
Na	305	309	306	307	312	307	311	308	309	mg/l
K	4.2	4.1	4.2	4.1	4.2	4.2	4.2	4.2	4.2	mg/l
dis Al	8.9	9.5	9	9.3	9.7	8.7	9.3	10.2	9.6	mg/l
dis Fe	<.1	<.1	<.1	.1	<.1	<.1	<.1	.12	<.1	mg/l
dis alk	545	550	550	535	545	545	565	550	560	mg/l CaCO3
SO4	48	48	48	48	48	48	48	48	48	mg/l as S
sulphide	...	...	...	...	...	...	...	...	.46	mg/l as S
DO	12.4	12.1	12.5	12.3	12.4	12.4	11.8	12.4	12.3	mg/l as O
DO	99.6	97.2	100.4	98.8	99.6	99.6	94.8	99.6	98.8	% as O
EC	1110	1120	1120	1120	1120	1120	1130	1130	1120	mhos/cm

KINGHORN LOCH - WATER BODY STATIONS for 30/10/81

station	27(1m)	25(BOT-.5m)	23(BOT-.5m)	23(1m)	21(BOT-.5m)	21(5m)	21(1m)	19(BOT-.5m)	19(1m)	
temp	6	6	6	6	6	6	6	6	6	C
pH	9.8	9.8	9.9	9.8	9.9	9.8	9.8	9.9	9.8	
dis Ca	5.4	4	4.4	5.1	4.5	4.7	3.9	4.5	4.5	mg/l
dis Mg	8.2	6.9	7.2	7.6	7.4	7.4	7.2	8	8.9	mg/l
Na	311	307	310	311	310	313	312	313	312	mg/l
K	4.2	4.1	4.2	4.2	4.2	4.2	4.2	4.2	4.2	mg/l
dis Al	9.6	8.7	8.9	9.2	9.9	9.5	9.4	9	8.9	mg/l
dis Fe	.18	<.1	<.1	<.1	<.1	<.1	<.1	<.1	.2	mg/l
dis alk	550	550	560	550	560	555	550	570	555	mg/l CaCO3
SO4	48	48	48	48	48	48	48	48	48	mg/l as S
sulphide	...	...	.36	...	.36	...	...	...	...	mg/l as S
DO	12.4	12.5	12.3	12.5	12	12.4	12.3	12.1	12.4	mg/l as O
DO	99.6	100.4	98.8	100.4	96.4	99.6	98.8	97.2	99.6	% as O
EC	1120	1120	1130	1120	1130	1130	1120	1120	1120	mhos/cm

KINGHORN LOCH - WATER BODY STATIONS for 30/10/81

station	17(BOT-.5m)	15(BOT-.5m)	15(5m)	15(1m)	13(BOT-.5m)	13(5m)	13(1m)	11(1m)	9(BOT-.5m)	
temp	6	6	6	6	6	6	6	7	6	C
pH	9.8	9.8	9.8	9.8	9.8	9.8	9.8	9.8	9.8	
dis Ca	5	5.1	4.6	3.9	4.8	4.4	5.1	4.8	5.1	mg/l
dis Mg	7.5	7.5	8.1	7.1	7.6	7.4	7.6	7.4	7.7	mg/l
Na	303	301	306	304	306	305	301	306	303	mg/l
K	4.2	4.2	4.3	4.2	4.2	4.2	4.2	4.1	4.1	mg/l
dis Al	8.8	9.4	9.3	9.4	9	9.1	8.4	8.3	8.7	mg/l
dis Fe	<.1	<.1	<.1	<.1	<.1	<.1	<.1	.17	<.1	mg/l
dis alk	555	565	550	550	550	550	550	555	550	mg/l CaCO3
SO4	48	48	48	48	48	48	48	48	48	mg/l as S
sulphide	...	.275	...	...	...	...	...	...	...	mg/l as S
DO	12.5	12.1	12.3	12.5	12.1	12.1	12.5	12.6	12.6	mg/l as O
DO	100.4	97.2	98.8	100.4	97.2	97.2	100.4	103.8	101.2	% as O
EC	1120	1120	1120	1120	1130	1130	1130	1120	1130	mhos/cm

KINGHORN LOCH - WATER BODY STATIONS for 30/10/81

station	9(1m)	7(BOT-.5m)	7(1m)	5(BOT-.5m)	5(1m)	3(BOT-.5m)	1(BOT-.5m)	
temp	6	6	6.5	6.5	6.5	6.5	7	C
pH	9.8	9.9	9.8	9.8	9.8	9.8	9.9	
dis Ca	5.1	5.1	5.1	4.5	4.5	5.1	5	mg/l
dis Mg	6.4	9.7	9.9	9.5	9.6	10	9.8	mg/l
Na	303	300	305	303	307	309	309	mg/l
K	4.2	4.3	4.1	4.2	4.2	4.2	4.1	mg/l
dis Al	9.1	8.7	9.4	9	9.2	9.4	9.2	mg/l
dis Fe	<.1	<.1	<.1	<.1	<.1	<.1	.21	mg/l
dis alk	555	560	555	545	555	540	550	mg/l CaCO3
SO4	48	48	48	48	48	48	48	mg/l as S
sulphide	...	.34	...	...	...	...	...	mg/l as S
DO	12.5	12.2	12.2	11.8	12.4	12.7	12.3	mg/l as O
DO	100.4	98	99.3	96	100.9	103.4	101.4	% as O
EC	1130	1140	1145	1150	1145	1150	1040	mhos/cm

KINGHORN LOCH - WATER BODY STATIONS
statistical appraisal - for 30/10/81

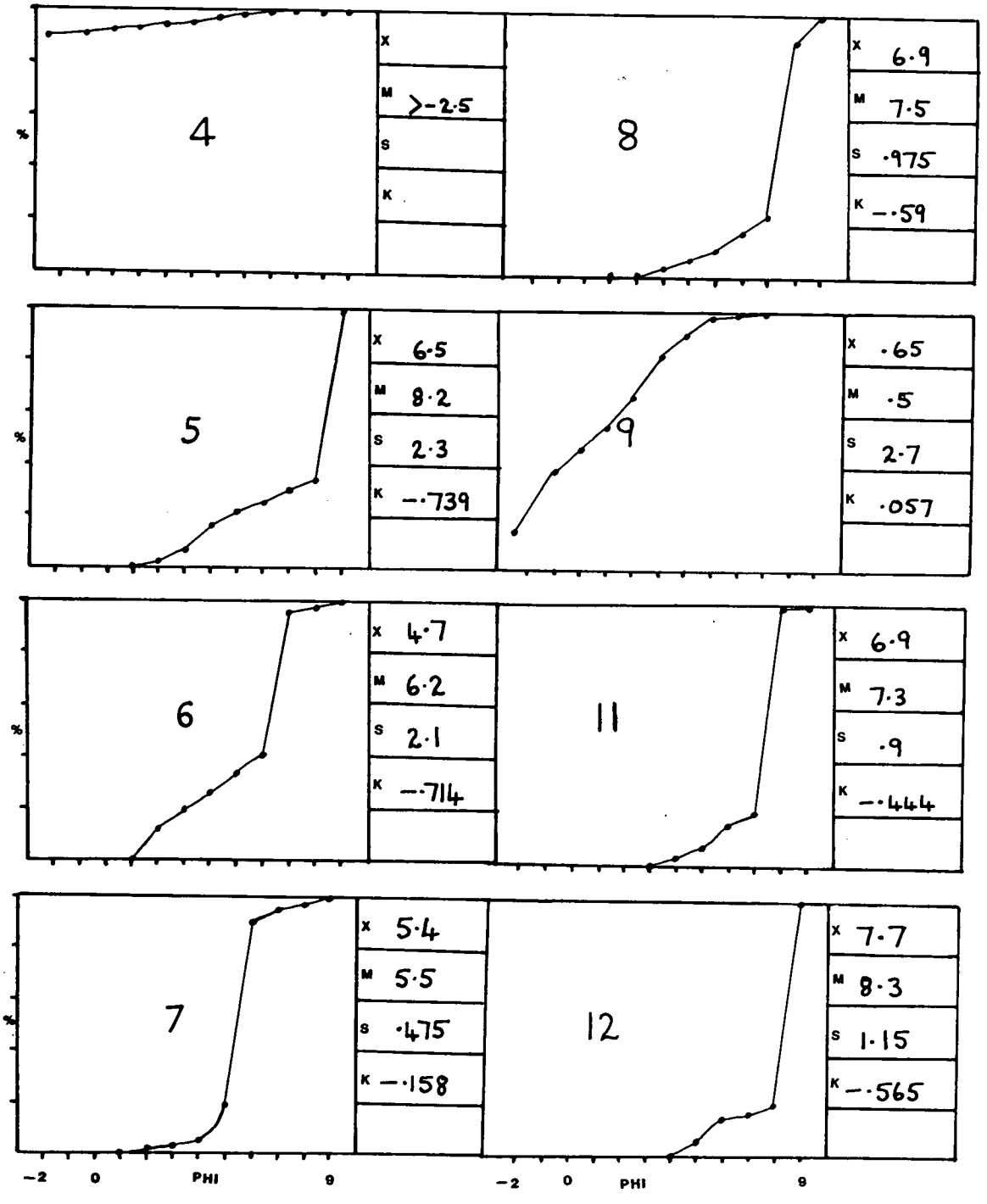
	samples	maximum	minimum	mean	std.dev.	n20	n10	n5	
temp	43	7.5	6	6.17442	.376129	0	1	6	C
pH	43	10.1	9.8	9.82559	.057054	1	5	31	
dis Ca	43	8.4	3.9	4.92791	.729749	2	8	34	mg/l
dis Mg	43	10	6.4	7.95115	.901761	1	5	20	mg/l
Na	43	399	298	309.326	14.484	0	1	3	mg/l
K	43	5.4	4.1	4.2186	.194155	0	1	3	mg/l
dis Al	43	11.5	8.1	9.11395	.574003	0	2	6	mg/l
dis Fe	43	.21	<.1	.069302	.047126	44	178	711	mg/l
dis alk	43	705	525	555.116	24.8687	0	1	3	mg/l CaCO3
SO4	43	54.3	44	48.0535	1.15018	0	0	1	mg/l as S
sulphide	7	.55	.275	.399285	.092214	5	20	82	mg/l as S
DO	43	12.7	11.8	12.3372	.215861	0	0	0	mg/l as O
DO	43	103.8	94.8	99.5488	1.98918	0	0	1	% as O
EC	43	1370	1040	1126.51	43.2798	0	1	2	mhos/cm

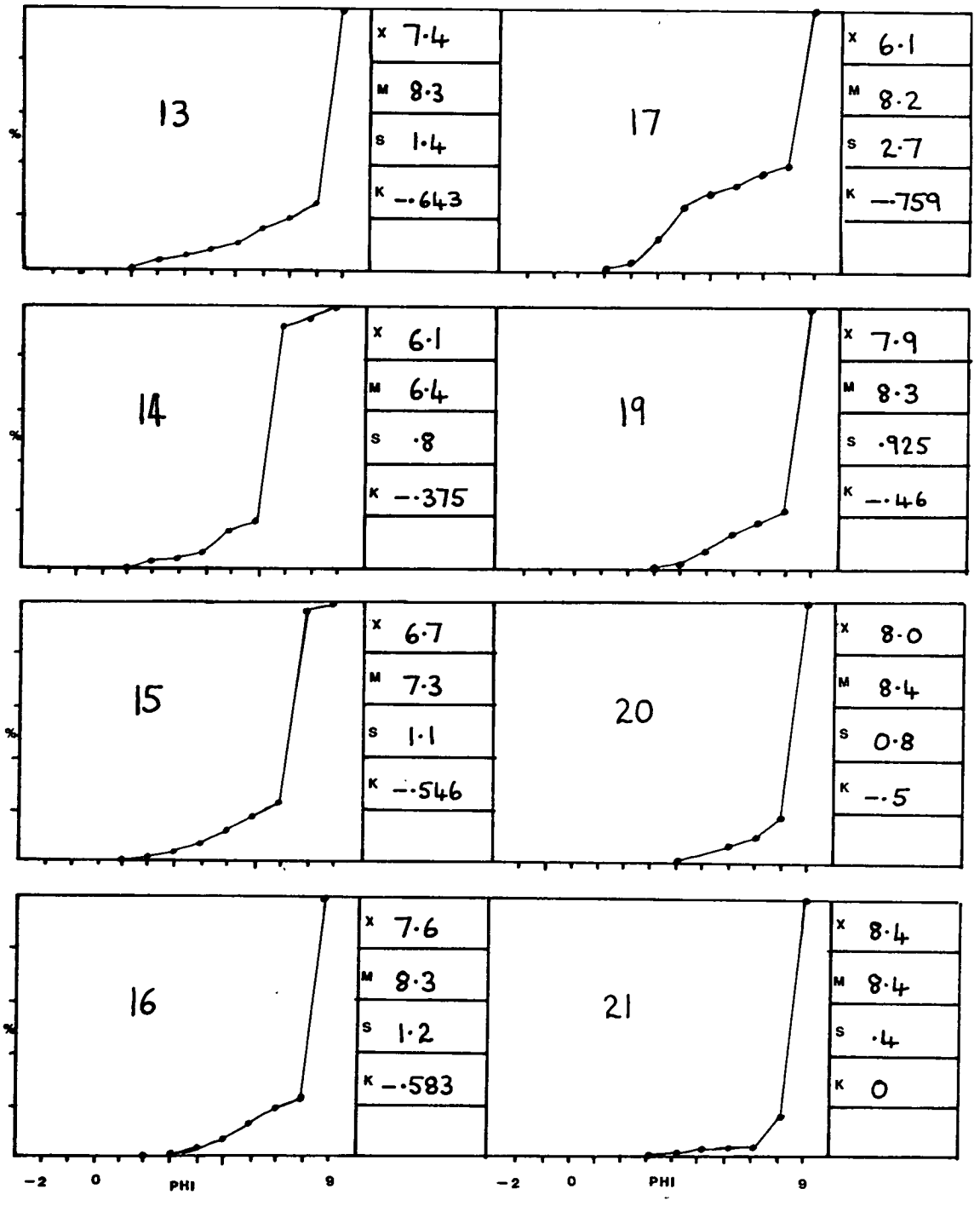
APPENDIX B

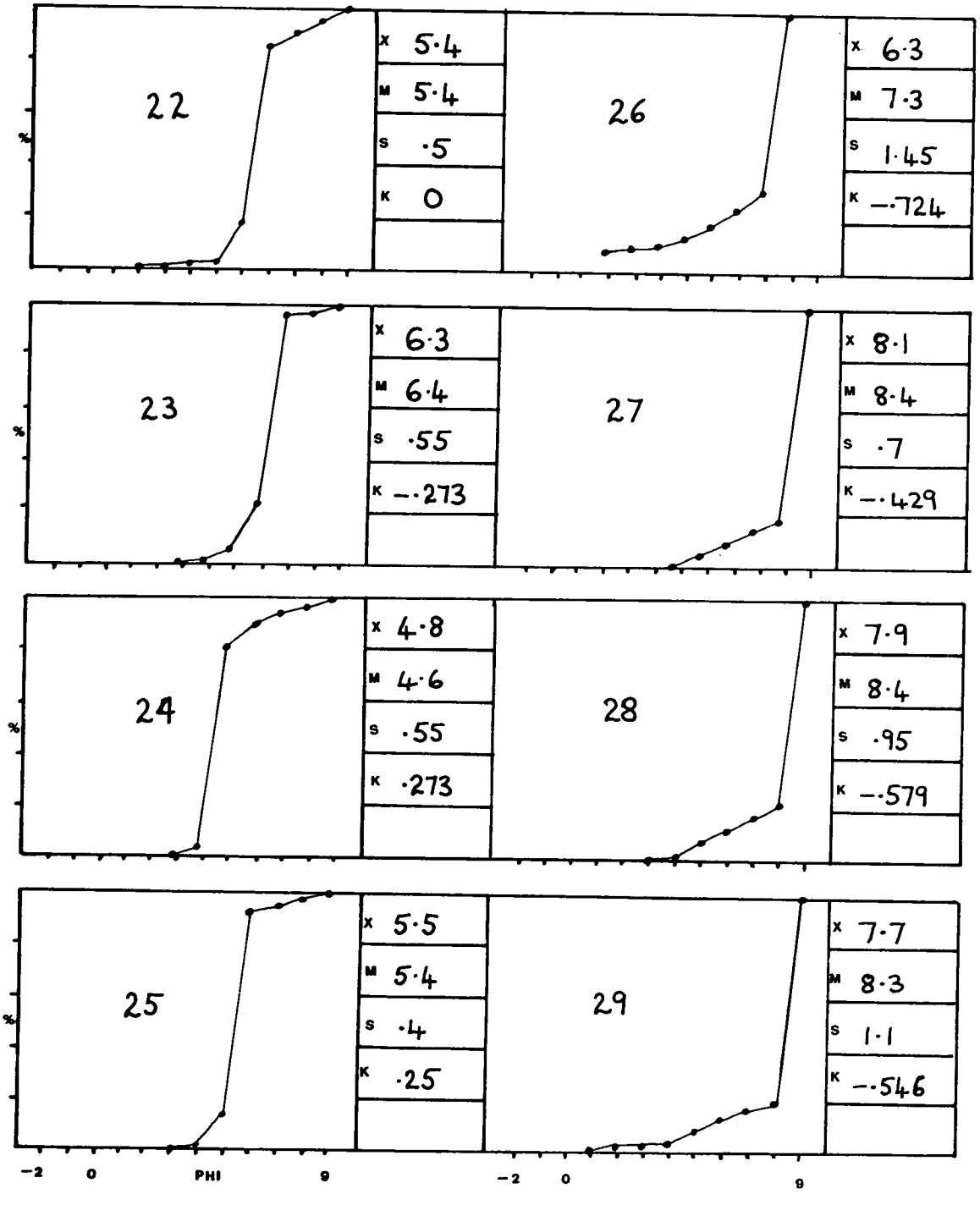
PHYSICAL DESCRIPTION OF SEDIMENT SURFACE

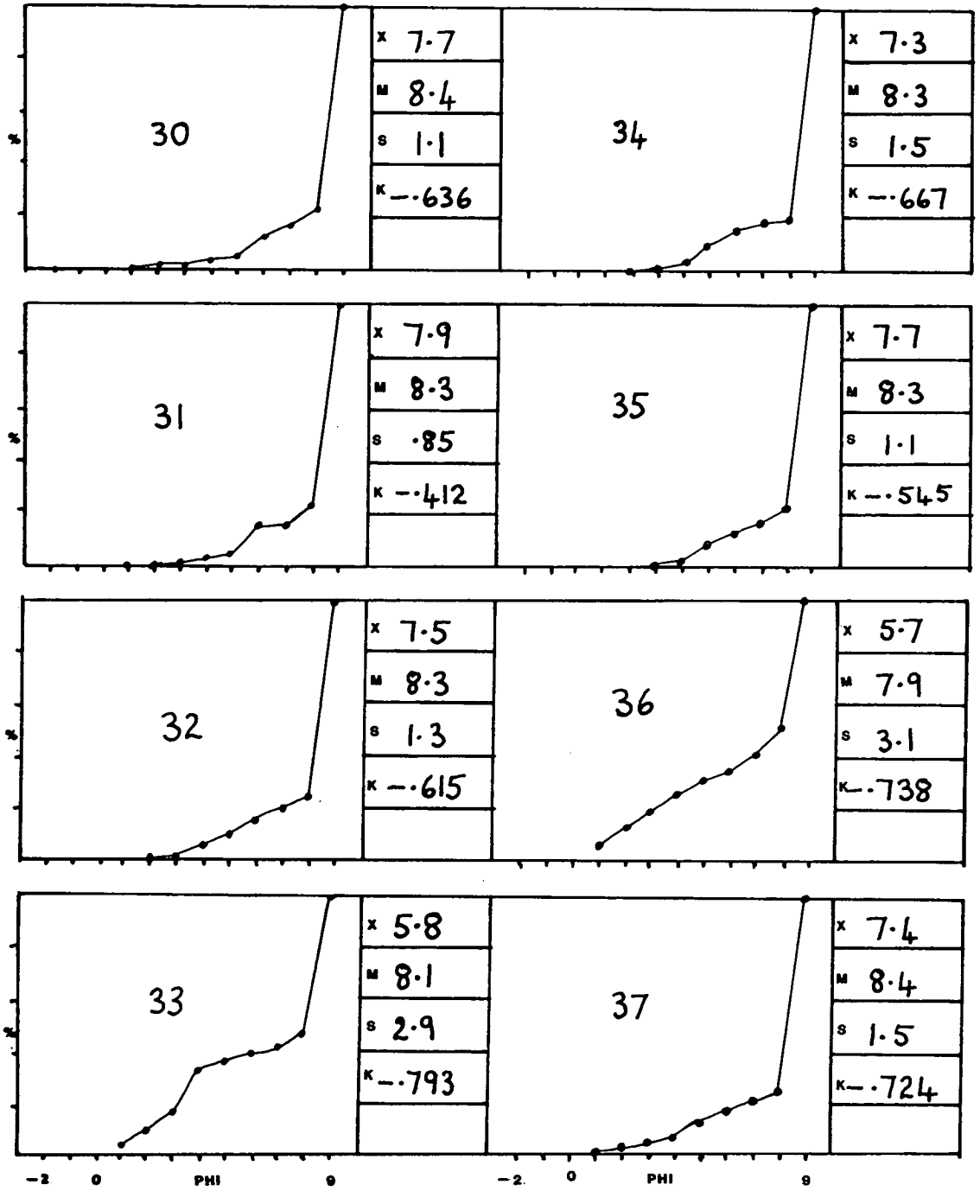
B.1. CUMULATIVE PERCENTAGE FREQUENCY CURVES.

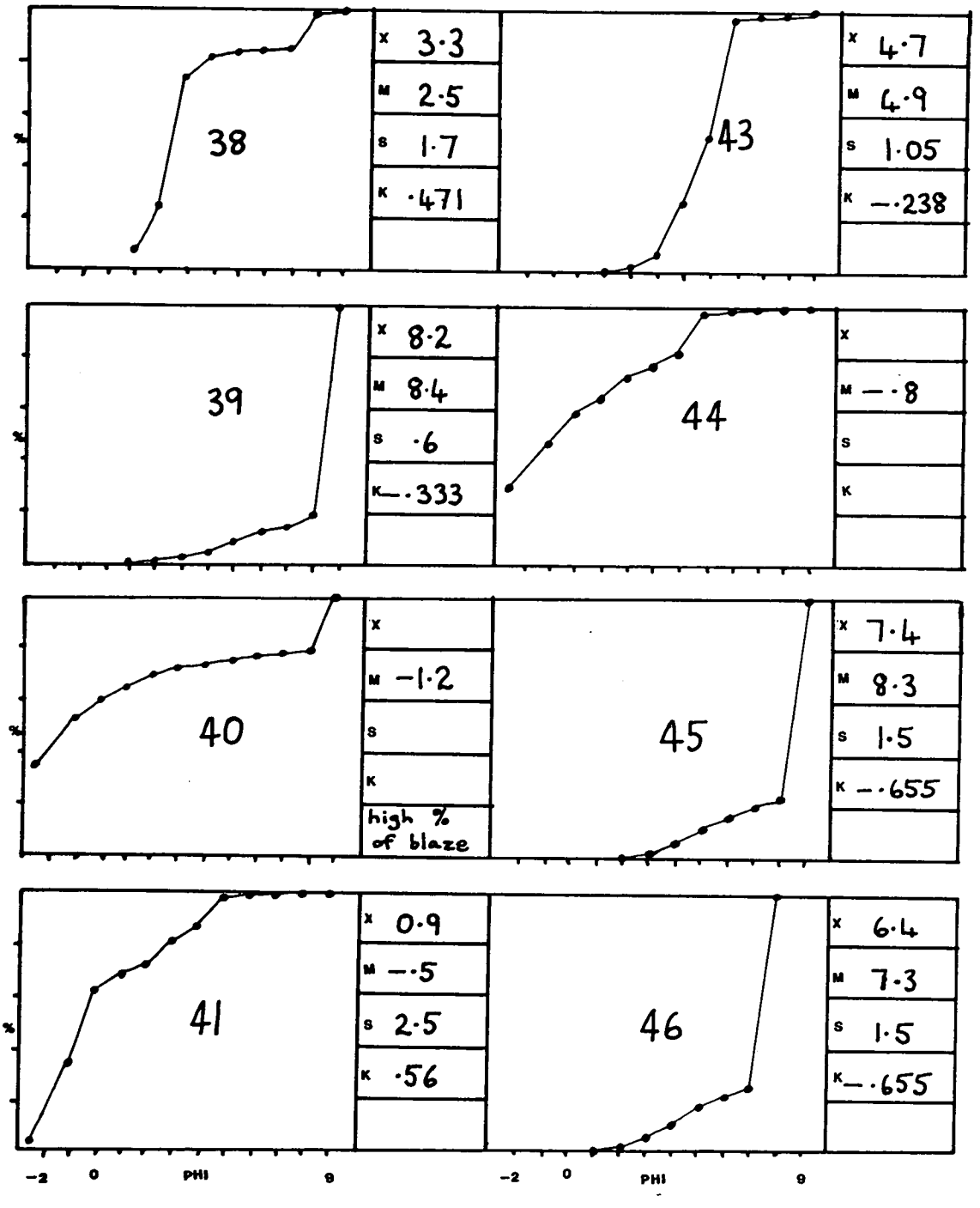
The figures compiled in this section represent the graphical display of the results from particle size analysis of the sediment surface and includes statistical parameters explained in Chapter 5.1.1.3.

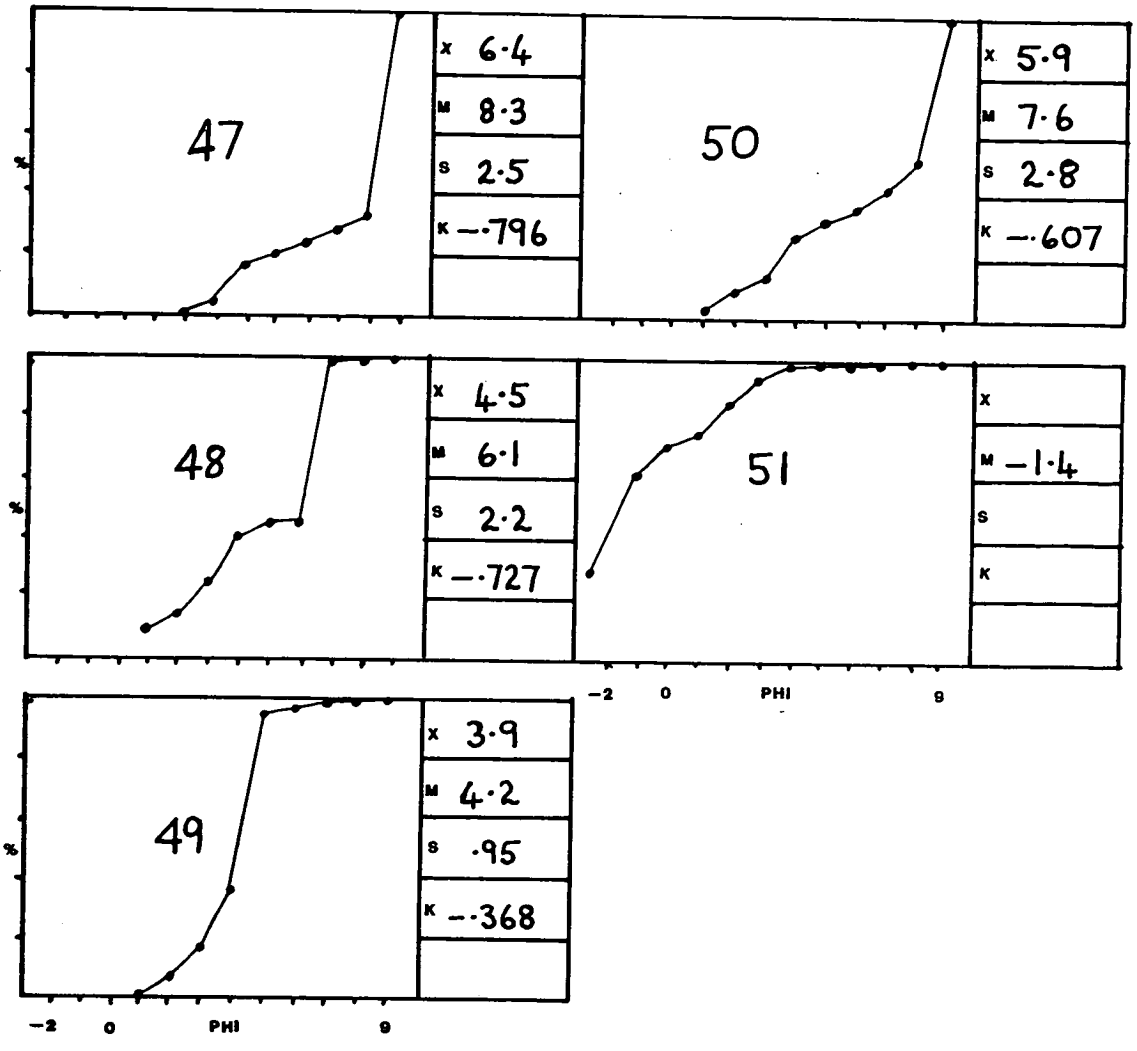

4
X
M >-2.5
S
K
8
X 6.9
M 7.5
S .975
K -.59
5
X 6.5
M 8.2
S 2.3
K -.739
9
X .65
M .5
S 2.7
K .057
6
X 4.7
M 6.2
S 2.1
K -.714
11
X 6.9
M 7.3
S .9
K -.444
7
X 5.4
M 5.5
S .475
K -.158
12
X 7.7
M 8.3
S 1.15
K -.565
%
-2
0
PHI
9


13
X 7·4
M 8·3
S 1·4
K −·643
17
X 6·1
M 8·2
S 2·7
K −·759
14
X 6·1
M 6·4
S ·8
K −·375
19
X 7·9
M 8·3
S ·925
K −·46
15
X 6·7
M 7·3
S 1·1
K −·546
20
X 8·0
M 8·4
S 0·8
K −·5
16
X 7·6
M 8·3
S 1·2
K −·583
21
X 8·4
M 8·4
S ·4
K 0
−2
0
PHI
9
−2
0
PHI
9


22
X 5·4
M 5·4
S ·5
K 0
26
X 6·3
M 7·3
S 1·45
K −·724
23
X 6·3
M 6·4
S ·55
K −·273
27
X 8·1
M 8·4
S ·7
K −·429
24
X 4·8
M 4·6
S ·55
K ·273
28
X 7·9
M 8·4
S ·95
K −·579
25
X 5·5
M 5·4
S ·4
K ·25
29
X 7·7
M 8·3
S 1·1
K −·546
%
−2
0
PHI
9


30
X 7·7
M 8·4
S 1·1
K −·636
34
X 7·3
M 8·3
S 1·5
K −·667
31
X 7·9
M 8·3
S ·85
K −·412
35
X 7·7
M 8·3
S 1·1
K −·545
32
X 7·5
M 8·3
S 1·3
K −·615
36
X 5·7
M 7·9
S 3·1
K −·738
33
X 5·8
M 8·1
S 2·9
K −·793
37
X 7·4
M 8·4
S 1·5
K −·724
−2
0
PHI
9
−2
0
PHI
9


38
X 3·3
M 2·5
S 1·7
K ·471
43
X 4·7
M 4·9
S 1·05
K —·238
39
X 8·2
M 8·4
S ·6
K —·333
44
X
M —·8
S
K
40
X
M —1·2
S
K
high % of blaze
45
X 7·4
M 8·3
S 1·5
K —·655
41
X 0·9
M —·5
S 2·5
K ·56
46
X 6·4
M 7·3
S 1·5
K —·655
-2
0
PHI
9
-2
0
PHI
9


47
X 6·4
M 8·3
S 2·5
K −·796
50
X 5·9
M 7·6
S 2·8
K −·607
48
X 4·5
M 6·1
S 2·2
K −·727
51
X
M −1·4
S
K
49
X 3·9
M 4·2
S ·95
K −·368
%
−2
0
PHI
9

B.2. GENERAL DESCRIPTION OF SEDIMENT SURFACE.

This section contains a decription of the sediment surface at each station as observed during the surveys of February 1981. It is a compilation of the visual appearance of the undisturbed surface as seen via the doors of the Van Veen grab (illustrated in Figure 5.1), observations on the debris not passing a 250 um sieve (during invertebrate separation), and the findings of particle-size analysis. Refer to Figure 4.1 to determine the location of each sampling station. The loch gave a mean pH value of 9.6 for the month, which was characterised by a prolonged period of calm weather.

Note that all "mud" was red-brown in colour unless otherwise stated. Any reference to Gastrapoda refers to occurences of shells only; no living individuals were found during any survey. Shells were generally in poor condition, being very fragile and thin.
m.d. = median diameter.

Station 1 to 3.

Rock or large stones without significant sediment.

Station 4.

Granule/pebble of 80-150 mm m.d.

Station 5 to 8.

Very poorly sorted muds (m.d. 4, 15, 22, and 6 um respectively), containing numerous cladocera eggs. A few sphaerium, ostraceda and lymnae shells were present. Station 8 contained detrital leaves. A very few chironomidae and chaoborus were seen.

Station 9.

Very poorly sorted coarse sand (m.d. 650 um), containing clodocera eggs and a few shells and some leaf debris. A very few chironomidae

were found.

Station 10.

Some coarse sand but mainly mineral encrusted, rotted macophyte debris of Polygonum amphibium. Chironomidae were abundant and other invertebrates were present.

Station 11.

Moderated sorted mud (m.d. 6 um), containing some fine, black, organic debris and small splinters of rotted wood. Numerous sphaerium shells but few cladocera eggs. Many empty chironomid tubes. A few chironomidae and chaoborus were found.

Station 12.

Poorly sorted mud (m.d. 3 um), containing similar material to station 11 but in much reduced numbers. A very few chironomidae and some chaoborus were observed.

Station 13.

Poorly sorted mud (m.d. 3 um), containing very little extraneous material. Chaoborus were abundant.

Station 14.

Anoxic mud, moderately sorted (m.d. 10 um), containing very little extraneous material. Chaoborus were abundant.

Station 15 to 16.

Poorly sorted mud (m.d. 6, 3 um respectively), containing very little debris except for a few very small lymnae and plentiful clodocera eggs. Abundant chaoborus were found though less so in station 16.

Station 17.

Very poorly sorted mud (m.d. 4 um) containing sand and stones to 20 mm. Very little debris. Chironomidae were present.

Station 18.

Rock, no sediment.

Station 19 to 20.

Moderately sorted mud (m.d. 3 um), containing little organic debris and very few shells or cladocera eggs; more numerous at station 20 where one caddis case was observed. Chaoborus were relatively abundant.

Station 21.

Anoxic mud, well sorted (m.d. 3 um), containing some detrital leaves and a number of sphaerium shells and clodocera eggs. Chaoborus were abundant.

Station 22.

Well sorted mud (m.d. 20 um), containing some large (8 mm) sphaerium shells, some leaves and cladocera eggs. Fairly abundant chaoborus were found.

Station 23.

Moderated well sorted mud (m.d. 10 um), similar to station 22 but containing some large pieces of mineral coated macrophyte debris. A few chaoborus were seen.

Station 24.

Moderately well sorted mud (m.d. 45 um); sample consisting mainly of mineral coated P.amphibium debris. Numerous clodocera eggs and ostracoda shells. Chironomidae were present.

Station 25.

Well sorted mud (m.d. 26 um); sample consisting mainly of mineral coated carex debris with few shells but abundant cladocera eggs. Abundant chironomidae were found together with some other invertebrates.

Station 26.

Poorly sorted mud (m.d. 7 um), similar, but less abundant, to station 25.

Station 27 to 28.

Moderately well sorted mud (m.d. 3 um), very little debris (more in station 28) and few clodocera eggs or shells. Chaoborus were present.

Station 29 to 30.

Poorly sorted mud (m.d. 3 um), very little dark, organic debris, some largish sphaerium shells and few cladocera eggs and ostraceda; station 30 contained chironomid tubes. Chaoborus and a few chironomidae were present.

Station 31.

Moderately sorted mud (m.d. 3 um), some fine organic debris with plentiful ostraceda shells and cladocera eggs. Moderate numbers of chaoborus and a few chironomidae seen.

Station 32.

Poorly sorted mud (m.d. 3 um), plentiful P.amphibium and leaf debris with a few chironomid tubes, cladocera eggs and ostraceda shells. Chironomidae were present.

Station 33.

Very poorly sorted mud, (m.d. 4 um), containing plentiful P.amphibium (much of it mineral coated) and leaf debris. Some chironomidae and a few chaoborus seen.

Station 34 to 37.

Poor or very poorly sorted mud (m.d. 3-4 um), with very little organic debris discernable. Abundant sphaerium and ostraceda shells and cladocera eggs and some chironomid tubes. A few chironomidae were present and chaoborus were present at stations 34 and

Station 38.

Anoxic, poorly sorted fine sand (m.d. 180 um), containing granules (approx. 10 mm) and some mineral coated macrophyte debris.

Station 39.

Anoxic, orange-red, moderately well sorted mud (m.d. 3 um), large amount of very light, friable mineral platelets. No real surface to sediment.

Station 40.

Very poorly sorted granules containing blaize (>20 mm) and assorted macrophyte litter much of it mineral coated. Some invertebrates were present.

Station 41.

Black mud and living macrophyte roots, mainly carex with P.amphibium; no mineral coating. Some invertebrates found.

Station 42.

Very poorly sorted, very coarse, dark sand (m.d. 1.4 mm) similar detritus to station 41. Very abundant small chironomidae and other invertebrates were found.

Station 43.

Poorly sorted mud (m.d. 32 um), containing granules to 20 mm and rotting organic material, mainly leaf. Few cladocera eggs or shells. Very abundant, very small chironomidae were seen.

Station 44.

Very coarse sand (m.d. 1.8 mm) on rock, containing a few cladocera eggs and several chironomid tubes. Abundant chironomidae were present.

Station 45 to 47.

Poor or very poorly sorted mud (m.d. 3, 7, 3 um respectively),

abundant dark organic detritus and mineral coated twigs. Abundant ostraceda shells and some cladocera eggs. Moderate numbers of chironomidae were found, a few chaoborus and a few other invertebrates.

Station 48.

Very poorly sorted mud (m.d. 16 um), with much organic material (mainly dumped oat grains) and granules up to 10 mm. No shells. Chironomidae were very abundant and procladius were present.

Station 49.

Moderated sorted mud (m.d. 55 um), very little debris, some chironomid tubes, and spiragyra. Chironomidae were present.

Station 50.

Very poorly sorted mud (m.d. 5 um), containing granules up to 10 mm and much undifferentiated plant and organic debris. Chironomidae were abundant.

Station 51.

Granule/pebble (m.d. 2.7 mm), very fine dark, organic detritus. Abundant, small chironomidae were observed.

APPENDIX C

PHYSICAL DESCRIPTION OF SEDIMENT CORES

Core profiles are shown for three sampling dates. pH (in situ) and moisture content profiles are also included. Cores taken in Spring 1983 were extracted after a period of prolonged turbulent weather while those for July 1983 were taken after calm weather. Note that this date is eight weeks after the diversion of the leachate, but no effect on loch water pH or chemistry was as yet apparent. A core was retrieved from station 39 in April 1985, by which time water pH and chemistry had very markedly improved.

Key to profiles.

diffuse surface material, water content >95% wet weight, of very fine, pale, bright red mud.

semi liquid to very soft fine, pale bright red mud.

very thin (1-2 mm) pale red "skin".

red brown, more colsolidated, mud, devoid of obvious detritus.

similar, but with a distinct grey hue.

similar, but pronounced dark grey colour.

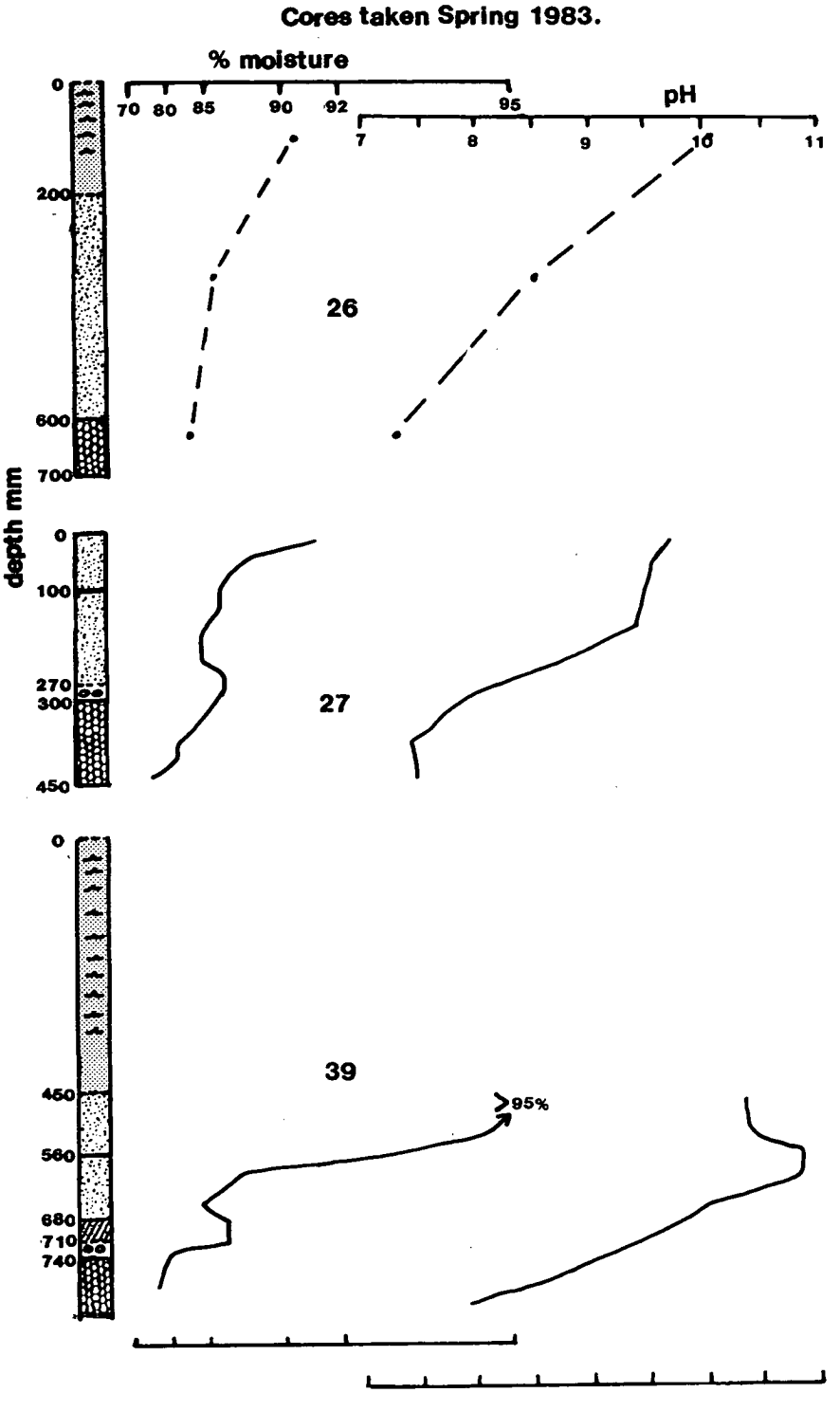
similar, but containing vegitative detritus and shells.

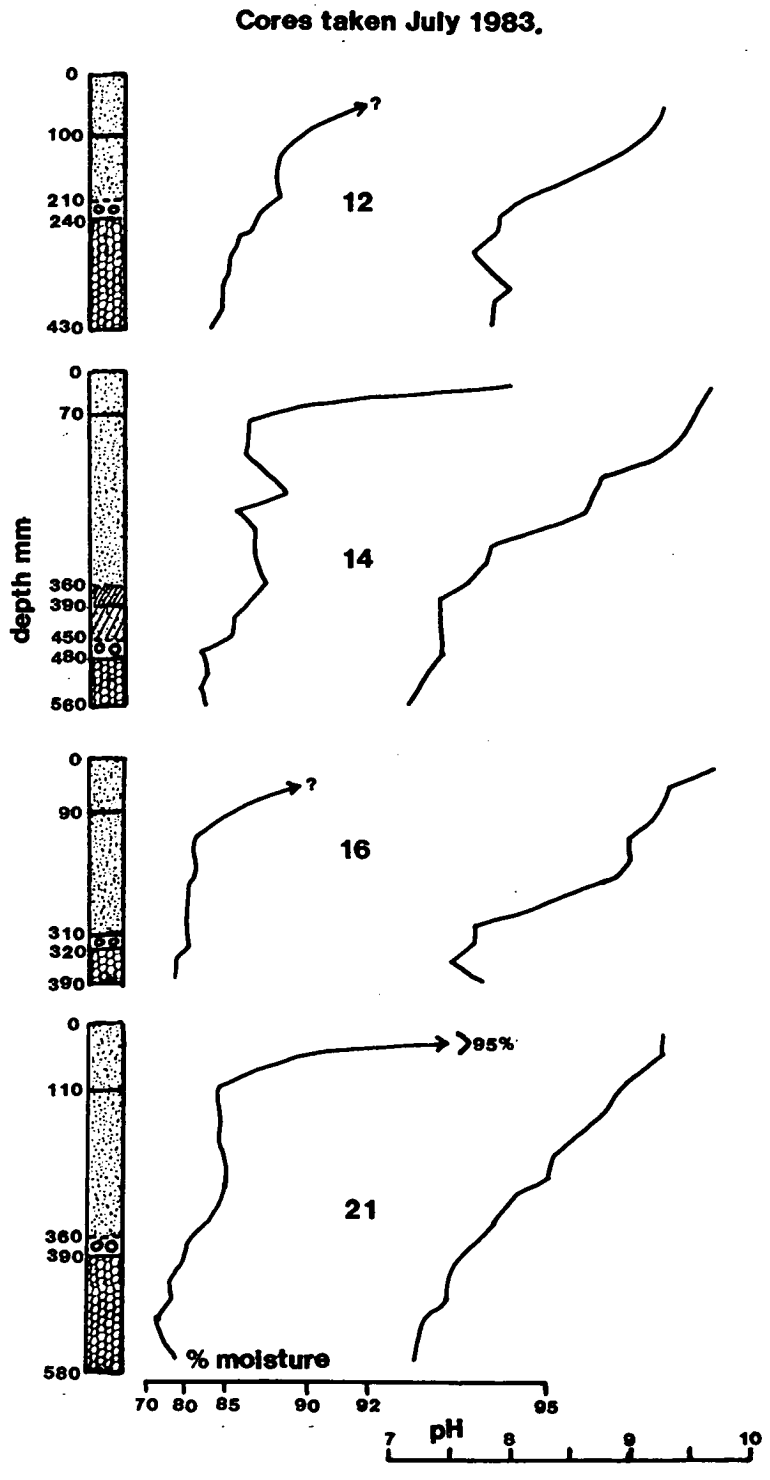
very dark brown fibrous material, containing many shells and vegitative detritus - the "natural" loch sediment.

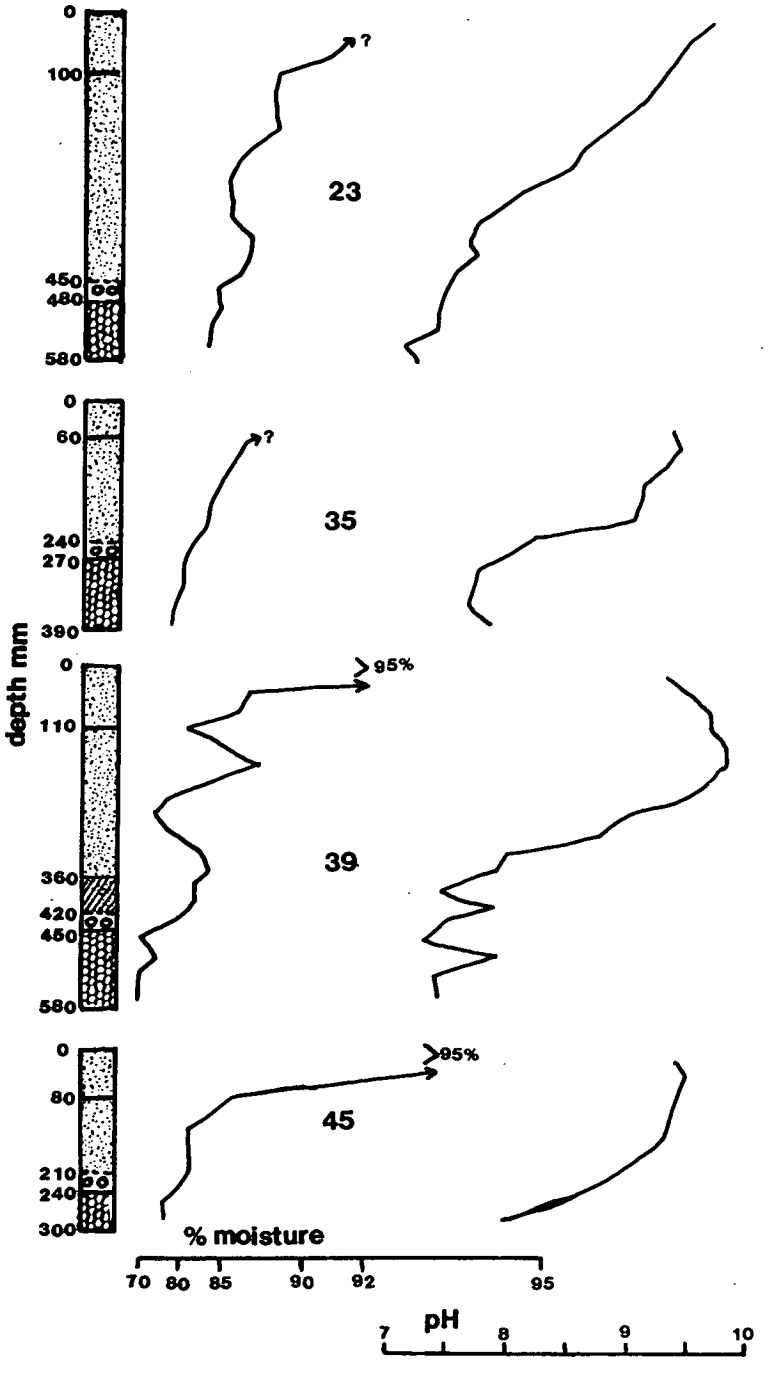
Notes.

--- progressive change from upper to lower type.

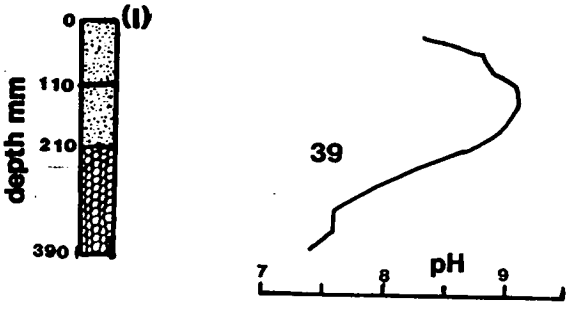
(I) Chironomus plumosus tubes in surface (April 1985, station 39).


Cores taken Spring 1983.
% moisture
70 80 85 90 92 95
pH
7 8 9 10 11
depth mm
0
200
600
700
26
0
100
270
300
450
27
0
450
560
680
710
740
39
>95%


Cores taken July 1983.
depth mm
0
100
210
240
430
12
?
0
70
360
390
450
480
560
14
0
90
310
320
390
16
?
0
110
360
390
580
21
>95%
% moisture
70 80 85 90 92 95
pH
7 8 9 10


depth mm
0
100
450
480
580
23
?
0
60
240
270
390
35
?
0
110
360
420
450
580
39
>95%
0
80
210
240
300
45
>95%
% moisture
70 80 85 90 92 95
pH
7 8 9 10

Core taken April 1985.



APPENDIX D

RESULTS OF ANALYSIS OF SEDIMENT CORES

Table D.1 tabulates the results of fused disc and pressed pellet analysis with C-H-N elemental analysis for cores at stations 14, 39, 39A, and 45.

Core 14

	14(0-3)	14(3-6)	14(6-9)	14(9-12)	14(12-15)	14(15-18)	14(18-21)	14(21-24)	14(24-27)	14(27-30)	
Si	...	4.099	4.051	5.316	6.398	4.818	5.779	7.227	9.614	11.13	%
Al	...	5.565	4.988	5.197	5.248	5.386	4.931	4.618	4.885	5.253	%
Fe	...	1.094	1.01	1.466	1.727	1.29	1.569	1.706	2.342	2.952	%
Mg	...	4.809	4.302	3.969	3.452	3.142	2.602	2.597	2.518	2.545	%
Ca	...	17.15	19.59	17.15	15.62	17.86	17.44	17.85	15.06	12.95	%
Na	...	.6268	.5056	.5738	.5068	.4687	.3956	.3562	.3677	.398	%
K	...	.0976	.1016	.1446	.1796	.1133	.1391	.1698	.2505	.2955	%
P	...	.1989	.1689	.1989	.2129	.2359	.2699	.2439	.2349	.2619	%
L.O.I.	...	45.2	43.4	43.1	42.8	44.4	43.8	40.8	38	35.1	%
O	...	20.74	20.7	21.44	21.91	20.69	21.02	22.6	24.74	26.34	%
Cl	...	0	0	0	0	0	0	0	0	0	mg/kg
Mo	...	0	4	16	32	22	26	12	8	7	mg/kg
Zr	...	43	39	52	62	52	56	63	78	102	mg/kg
Y	...	6	6	7	9	8	9	9	12	14	mg/kg
Sr	...	748	804	721	626	704	669	630	498	461	mg/kg
Rb	...	7	7	8	10	7	9	11	14	16	mg/kg
Th	...	0	0	0	0	0	0	0	2	2	mg/kg
Pb	...	20	22	28	38	29	33	41	56	65	mg/kg
As	...	747	653.9	560.9	440.9	435.6	366.4	263.1	230.8	218.8	mg/kg
Zn	...	53	54	78	105	75	92	108	153	165	mg/kg
Cu	...	49	39	42	46	38	43	53	56	55	mg/kg
Ni	...	35	33	43	54	41	51	60	74	87	mg/kg
Mn	...	278	317	488	690	548	689	1127	1347	1480	mg/kg
Cr	...	137	129	136	125	95	101	125	152	182	mg/kg
V	...	2554	1330	1249	1086	1330	1207	644	547.6	515.6	mg/kg
Ba	...	107	146	143	166	142	179	204	225	252	mg/kg
Ti	...	1232	1192	1648	2142	1540	1750	2098	3057	3865	mg/kg
I	...	403	407	409	417	410	389	393	336	298	mg/kg
S	...	1108	1336	3083	4934	3071	4208	4678	5720	6658	mg/kg
Br	...	29	26	33	37	33	32	39	42	52	mg/kg
org C	9.77	7.93	5.06	7.54	8.33	6.95	8.24	6.82	7.36	7.77	%
inorg C	2.77	4.96	6.08	5.02	4.59	5.34	5.15	5.1	4.18	3.58	%
N	1.01	.92	.57	.71	.81	.81	.98	.8	.88	.88	%
moisture	94.5	90.2	86.9	86.9	86.9	88	88.9	85.7	87.4	87.3	% wet wt.

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Core 14

	14(30-33)	14(33-36)	14(36-39)	14(39-42)	14(42-45)	14(45-48)	14(48-51)	14(51-54)	14(54-56)	
Si	13.82	14.02	15.23	16.27	16.05	17.2	17.99	18.48	17.72	%
Al	5.077	4.86	4.702	4.885	4.753	5.068	5.301	4.992	4.619	%
Fe	3.433	3.603	4.031	4.515	4.666	5.048	5.412	5.398	4.726	%
Mg	2.364	2.59	2.471	2.576	2.505	2.723	2.791	2.645	2.497	%
Ca	10.32	9.527	8.544	8.064	7.217	7.041	6.508	6.062	8.056	%
Na	.4125	.4674	.4885	.4212	.3805	.4242	.3699	.3102	.2529	%
K	.3814	.4243	.4985	.5758	.5669	.6253	.6522	.6103	.5642	%
P	.2159	.1649	.1469	.1289	.1249	.1229	.1269	.1169	.1129	%
L.O.I.	33.2	33.1	32.3	30.3	29.9	28.4	26.4	27.1	29.4	%
O	28.29	28.21	29.2	30.66	29.95	31.84	32.96	32.89	32.04	%
Cl	0	0	0	0	0	0	0	0	0	mg/kg
Mo	6	12	11	7	4	1	0	0	0	mg/kg
Zr	105	115	122	134	128	139	147	138	123	mg/kg
Y	15	18	18	19	19	19	20	19	17	mg/kg
Sr	402	329	314	284	271	277	266	245	268	mg/kg
Rb	21	25	26	29	28	30	31	29	26	mg/kg
Th	2	1	1	3	0	2	2	2	1	mg/kg
Pb	78	97	95	97	91	86	82	65	52	mg/kg
As	181.7	108.6	64.83	47.08	33.13	22.54	16.44	16.54	15.4	mg/kg
Zn	194	222	213	206	191	172	152	127	95	mg/kg
Cu	60	62	58	57	52	55	53	46	37	mg/kg
Ni	102	123	133	147	143	154	159	152	137	mg/kg
Mn	1276	1064	939	946	972	970	873	787	808	mg/kg
Cr	194	197	183	194	182	198	203	193	172	mg/kg
V	486.5	406.4	272.7	199	179.1	176.7	172.6	173.7	154.5	mg/kg
Ba	260	315	285	321	308	332	361	362	317	mg/kg
Ti	4380	5374	5815	6505	6466	7034	7406	7124	6459	mg/kg
I	253	211	203	184	178	173	163	152	189	mg/kg
S	8519	13194	19667	20553	23842	20402	18204	21732	15835	mg/kg
Br	56	58	57	53	56	66	65	62	63	mg/kg
org C	8.19	8.37	8.99	8.1	7.7	7.04	7.03	6.49	6.29	%
inorg C	2.64	2.42	2.14	2.01	1.97	1.78	1.46	1.39	2.15	%
N	1.17	.97	.98	.87	.93	.73	.7	.62	.71	%
moisture	87.5	88	87.1	85.6	85.3	82	82.9	82	83.2	% wet wt.

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Core 39

	39(0-3)	39(3-6)	39(6-9)	39(9-12)	39(12-15)	39(15-18)	39(18-21)	39(21-24)	39(24-27)	39(27-30)	
Si	3.385	3.378	3.22	2.905	2.898	2.849	5.143	4.361	3.685	9.478	%
Al	5.256	5.174	4.795	4.391	4.403	4.65	5.625	5.02	5.823	5.12	%
Fe	2.156	2.502	2.579	2.573	2.575	2.619	3.064	2.444	1.568	2.494	%
Mg	5.826	5.535	4.91	4.498	4.52	5	5.31	4.456	5.65	3.696	%
Ca	17.94	18.33	19.2	21.4	21.51	19.52	17.72	19.16	16.68	14.5	%
Na	0	.492	.5411	.6057	.531	.6245	.6913	.5094	.4557	.5061	%
K	.1131	.1435	.1407	.1295	.132	.1164	.2711	.1938	.102	.3158	%
P	.237	.2389	.2259	.2189	.2199	.2329	.2119	.195	.226	.165	%
L.O.I.	41.5	41.5	41.5	41.4	41	42.7	36.9	40.4	43.5	35.9	%
O	20.53	21.21	20.67	20.56	20.6	20.35	23.57	21.74	21.07	25.41	%
Cl	...	0	0	0	0	0	0	0	0	0	mg/kg
Mo	...	5	0	0	0	1	9	2	4	6	mg/kg
Zr	...	84	100	103	109	86	114	91	67	108	mg/kg
Y	...	9	9	9	9	9	12	9	9	13	mg/kg
Sr	...	794	827	895	847	809	770	896	795	721	mg/kg
Rb	...	8	11	10	11	15	19	11	6	14	mg/kg
Th	...	3	4	3	3	2	2	0	0	0	mg/kg
Pb	...	23	26	22	34	35	30	32	35	43	mg/kg
As	...	790.8	678.9	678.6	883.3	977.7	932.3	733	917.1	564.9	mg/kg
Zn	...	52	49	44	59	60	60	51	53	75	mg/kg
Cu	...	29	26	23	38	35	34	28	42	50	mg/kg
Ni	...	52	42	40	47	42	49	38	35	65	mg/kg
Mn	...	522	468	449	626	510	490	358	455	715	mg/kg
Cr	...	120	126	131	160	99	127	107	102	124	mg/kg
V	...	293.6	275.8	247.9	306.4	326.5	274.4	289.4	371.6	330.3	mg/kg
Ba	...	79	84	97	98	107	148	129	136	217	mg/kg
Ti	...	2062	2303	2272	2565	1976	2685	1991	1448	3028	mg/kg
I	...	413	381	398	370	343	349	393	362	332	mg/kg
S	...	1162	832.2	114.8	769	1708	2705	2114	2531	7476	mg/kg
Br	...	26	23	21	27	30	30	29	38	39	mg/kg
org C	4.46	4.3	3.8	3.36	4.42	4.58	4.45	4.63	6.32	7.6	%
inorg C	5.41	5.67	5.99	6.59	5.88	5.94	5.04	5.61	4.91	3.81	%
N	.29	.29	.21	.18	.25	.16	.28	.28	.46	.45	%
moisture	98.7	87.3	86.5	80.8	84.2	87.7	83.8	76.1	74.1	77.3	% wet wt.

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Core 39

	39(30-33)	39(33-36)	39(36-39)	39(39-42)	39(42-45)	39(45-48)	39(48-51)	39(51-54)	39(54-58)	
Si	13.09	15.92	21.01	17.04	17.28	17.36	17.98	22.36	22.9	%
Al	5.107	4.726	3.797	4.677	5.18	5.375	5.328	4.566	4.602	%
Fe	3.465	4.523	4.207	4.142	4.838	5.398	5.091	3.841	3.882	%
Mg	2.983	2.568	2.055	2.691	2.692	2.757	2.666	2.295	2.255	%
Ca	7.645	5.228	3.167	4.866	3.827	3.892	3.035	2.607	2.433	%
Na	.6407	.6521	.5395	.5667	.5436	.4929	.4862	.4226	.3926	%
K	.4993	.5711	.5664	.5614	.6496	.6892	.7379	.7212	.7362	%
P	.1339	.1169	.0939	.1199	.114	.114	.108	.093	.09	%
L.O.I.	35.2	33.3	29.4	32.6	31.9	30.7	31.3	26.2	25.3	%
O	26.86	28.99	32.6	29.99	30.67	31.27	31.43	34.69	35.26	%
Cl	0	0	0	0	0	0	7.615	0	0	mg/kg
Mo	23	16	14	10	3	0	0	0	0	mg/kg
Zr	144	167	156	156	157	154	152	173	185	mg/kg
Y	19	21	17	20	21	20	20	20	18	mg/kg
Sr	329	224	226	233	232	243	282	223	185	mg/kg
Rb	29	29	22	28	32	31	28	26	26	mg/kg
Th	1	0	1	1	2	2	3	0	0	mg/kg
Pb	66	70	44	59	67	62	55	45	28	mg/kg
As	332.5	257.4	253.6	150.6	69.78	60.32	108	52.29	41.31	mg/kg
Zn	146	154	104	122	135	122	106	85	71	mg/kg
Cu	54	53	40	51	50	45	41	32	27	mg/kg
Ni	117	132	108	135	148	143	129	117	108	mg/kg
Mn	626	544	478	541	548	550	486	415	362	mg/kg
Cr	198	207	169	211	222	223	211	213	197	mg/kg
V	328.7	204.5	175.8	219.8	207.1	199	199.5	176.9	151.9	mg/kg
Ba	320	348	307	383	410	396	336	366	337	mg/kg
Ti	6185	7103	5870	7455	7895	8101	7376	7681	7000	mg/kg
I	159	100	100	89	97	110	135	94	78	mg/kg
S	22835	40651	38874	30083	27034	29180	19404	9359	6066	mg/kg
Br	65	67	65	75	77	70	66	54	37	mg/kg
org C	11.56	11.83	11.04	11.35	11.36	11.01	11.15	9.47	8.15	%
inorg C	1.96	.98	.51	1.19	.52	.79	.41	.47	.29	%
N	.75	.81	.8	.79	.91	.88	.91	.71	.56	%
moisture	82.4	83.6	81.5	81.6	79.1	67.8	74.8	68.7	68.3	% wet wt.

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Core 39A

	39A(0-45)	39A(45-48)	39A(48-51)	39A(51-54)	39A(54-57)	39A(57-60)	39A(60-63)	39A(63-66)	39A(66-69)	39A(69-72)	
Si	2.897	3.743	3.787	3.758	3.349	2.799	2.877	3.375	3.923	3.384	%
Al	4.43	6.162	6.07	6.139	5.903	4.367	4.114	4.504	5.008	5.167	%
Fe	2.516	2.801	2.721	2.744	3.582	2.515	2.261	1.808	1.999	1.613	%
Mg	4.181	6.463	6.427	6.511	5.744	4.452	4.401	4.752	4.927	4.721	%
Ca	7.171	11.64	12.38	12.68	13.57	20.16	19.29	17.5	16.94	17.82	%
Na	1.701	.9655	.7397	.856	1.213	.8762	.7424	.6058	.6484	.4113	%
K	.0059	.0949	.1039	.1085	.1098	.0923	.1147	.133	.1347	.0916	%
Ti	.231	.264	.255	.257	.327	.222	.186	.151	.179	.143	%
Mn	.033	.041	.041	.044	.038	.036	.031	.033	.045	.042	%
P	.2986	.3636	.3567	.3708	.3588	.2639	.2249	.1999	.2159	.2139	%
L.O.I.	43.4	43.2	43.1	43.1	42.2	42.9	44.6	46	44.1	45	%
O	15.13	20.94	21.05	21.33	21.01	20.02	19.27	19.41	20.52	19.98	%
moisture	99.7	96.8	95.7	94.6	93.4	88	86.1	84.3	86.4	86.6	% wet wt.

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Core 39A

	39A(72-75)	39A(75-78)	39A(78-81)	39A(81-85)	
Si	3.928	4.546	10.65	14.19	%
Al	4.662	4.18	4.401	4.216	%
Fe	1.484	1.404	2.566	3.781	%
Mg	3.476	3.009	3.024	2.349	%
Ca	20.85	22.09	13.25	7.095	%
Na	.2653	.2341	.2836	.4517	%
K	.1055	.1327	.3037	.4998	%
Ti	.143	.151	.33	.494	%
Mn	.049	.057	.07	.045	%
P	.1749	.176	.139	.106	%
L.O.I.	42.9	41.9	34.4	35.7	%
O	20.38	20.81	25.08	26.73	%
moisture	80.4	78.3	77.6	76.5	% wet wt.

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Core 45

	45(0-3)	45(3-6)	45(6-9)	45(9-12)	45(12-15)	45(15-18)	45(18-21)	45(21-24)	45(24-27)	45(27-30)	
Si	7.23	7.633	7.964	8.751	9.86	10.87	12.95	15.87	17.57	17.73	%
Al	5.099	5.224	5.211	5.429	5.267	5.239	5.268	5.469	5.557	5.251	%
Fe	1.976	2.117	2.206	2.492	2.768	2.986	3.462	4.454	5.117	5.581	%
Mg	3.99	3.93	3.652	3.441	3.265	3.172	3.038	3.12	3.23	3.074	%
Ca	16.36	16.91	16.7	15.9	14.25	14.12	12.09	8.809	7.394	7.921	%
Na	.2957	.3499	.3768	.325	.4067	.4717	.4727	.6343	.6387	.5914	%
K	.2114	.2277	.2396	.2691	.3184	.3524	.4274	.5895	.6588	.6528	%
P	.1377	.1428	.1449	.1549	.1579	.1629	.1519	.1419	.128	.119	%
L.O.I.	37.7	37.8	37.6	36.5	36.8	34.2	31.2	27	24.9	22.9	%
O	23.35	24.21	24.36	25.14	25.68	26.85	28.6	31.46	33.34	33.54	%
Cl	...	0	0	0	0	0	0	0	0	0	mg/kg
Mo	...	0	0	0	0	0	0	0	0	1	mg/kg
Zr	...	71	74	78	87	94	109	132	153	157	mg/kg
Y	...	10	9	11	11	13	14	18	20	19	mg/kg
Sr	...	645	626	610	527	503	436	374	314	311	mg/kg
Rb	...	14	15	14	18	21	24	30	32	30	mg/kg
Th	...	0	0	0	1	1	0	3	3	0	mg/kg
Pb	...	35	37	40	44	54	66	87	96	90	mg/kg
As	...	384.2	378.9	332.3	232.6	188.6	136.6	108.7	67.94	64.91	mg/kg
Zn	...	105	111	120	143	163	189	216	223	209	mg/kg
Cu	...	33	36	38	46	52	54	60	58	54	mg/kg
Ni	...	68	71	78	91	98	112	141	162	172	mg/kg
Mn	...	676	743	814	919	996	1071	1108	1288	1284	mg/kg
Cr	...	128	136	138	156	164	183	210	243	249	mg/kg
V	...	248.2	226.8	212.4	187.9	227.9	249.8	295	294.4	255.3	mg/kg
Ba	...	167	173	176	217	220	239	303	364	365	mg/kg
Ti	...	2812	2901	3147	3770	4133	4835	6093	7471	7666	mg/kg
I	...	625	668	686	551	462	393	287	212	206	mg/kg
S	...	1641	1694	1809	1856	2520	4655	12624	19506	19606	mg/kg
Br	...	50	57	64	70	67	67	55	49	52	mg/kg
org C	...	4.58	3.18	6.6	6.94	6.92	7.32	7.84	7.17	6.16	%
inorg C	...	6.68	5.08	4.91	4.4	4.23	3.61	2.41	2.17	1.98	%
N	...	.59	.59	.63	.63	.63	.67	.66	.58	.52	%
moisture	95.9	92.2	86.7	84.1	81.1	81.2	81.5	80.1	76.7	77.2	% wet wt.

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APPENDIX E

COMPUTER PROGRAMS

TABLE E.1. "KLOCHCOEFF" a computer program for the calculation of Pearson's correlation coefficients for aqueous chemistry.

KLOCHCOEFF

```
0010 !KLOCHCOEFF
0015 TAB =5
0020 RESTORE
0030 DATA 6,7,9,11,12,13,15,17,18,19,25,29,30,31,32,35,36,37,38,44,45,47
0040 MAT READ R(22)
0050 DATA "pH","diss Ca","diss Mg","Na","K","diss Al","diss Fe","tot As"
0060 DATA "Tot V","tot Mn","diss alk","Cl","SO4","SiO2","NO3","NH3","F","PO4","E.C.","S.S.","chlorophyll"
0080 OPEN FILE (0,2),"out.mx"
0090 GPOS FILE (0),P
0100 LET P=P/200-1
0110 DIM M(50),N(22,22)
0120 FOR I=1 TO 22
0130   FOR J=1 TO 22
0140     LET N(I,J)=-9999
0150   NEXT J
0160 NEXT I
0170 FOR I=1 TO 21
0180   FOR J=I+1 TO 22
0190     PRINT I;":";J,
0200     LET N=0 !no of co-results
0210     LET S=0 !sumxy
0220     LET S1=0 !sumx
0230     LET S2=0 !sumy
0240     LET S3=0 !sumxx
0250     LET S4=0 !sumyy
0260     FOR K=0 TO P
0270       SPOS FILE (0),K*200
0280       MAT READ FILE (0),M
0290       LET E=0
0300       LET Y=M(R(I))
0310       GOSUB 0710
0320       LET X=Y
0330       LET Y=M(R(J))
0340       GOSUB 0710
0350       IF E THEN GOTO 0430
0360       IF J=27 THEN IF Y<>-9999 THEN LET Y=LOG(Y)*.434294 !log10(chlorophyll)
0370       LET S=S+X*Y
0380       LET S1=S1+X
0390       LET S2=S2+Y
0400       LET S3=S3+X*X
0410       LET S4=S4+Y*Y
0420       LET N=N+1
0430     NEXT K
0440     IF N<5 THEN GOTO 0480
0450     LET X=S-S1*S2/N
0460     LET Y=(S3-S1*S1/N)*(S4-S2*S2/N)
0470     LET N(I,J)=INT(X/SQR(Y)*1000+.5)
0475     PRINT N(I,J)
0480   NEXT J
```

KLOCHCOEFFcont

```
0495 OPEN FILE (1,1),"loch.cf"
0496 MAT WRITE FILE (1),N
0500 CLOSE
0501 OPEN FILE (1,3),"loch.cf"
0502 DIM N(22,22)
0503 MAT READ FILE (1),N
0505 RESTORE 0050
0510 PRINT "printout occuring"
0520 OPEN FILE (0,1),"$lpt"
0530 PRINT FILE (0),"<13><27><Correlation coefficients (x1000) for loch water 1981-1983<27>="
0540 PRINT FILE (0),"<13><13>              temp pH tCa dCa tMg dMg  Na  K  tAl dAl tFe dFe ";
0550 PRINT FILE (0)," As  V   Mn talkdalk Cl SO4  Si NO3 NH3  F  PO4  EC  SS c'phyll"
0560 PRINT FILE (0),"============ ==== == === === === ===  ==  =  === === === === ";
0570 PRINT FILE (0)," ==  =   == ======== == ===  == === ===  =  ===  ==  == ======="
0580 FOR I=1 TO 21
0590   READ D$
0600   PRINT FILE (0),D$; TAB(11);"|";
0610   FOR J=2 TO 22
0620     LET A$="   "
0630     IF N(I,J)<>-9999 THEN LET A$=STR$(N(I,J))
0640     PRINT FILE (0),A$,
0650   NEXT J
0660   PRINT FILE (0)
0670 NEXT I
0680 PRINT FILE (0),"<13><13>";STR$(SYS(1));"/";STR$(SYS(2));"/";STR$(SYS(3)-1900)
0690 CLOSE
0695 TAB =14
0700 STOP
0710 IF Y=-9999 THEN LET E=1
0720 IF Y<0 THEN LET Y=(-Y)/2
0730 IF Y>9000 THEN LET Y=Y-90000
0740 RETURN
```

dated: 14 / 10 / 1985

TABLE E.2. "CLUSTER" and "CLUSTER2" computer programs for the multivariate correlation between the segments of a core and between cores.

```
CLUSTER
0010 !Cluster
0020 OPEN FILE (1,1),"CORE.MX"
0030 OPEN FILE (0,3),"14.MX"
0040 DIM R(37),M(18,37)
0050 MAT READ FILE (0),R,M
0060 MAT WRITE FILE (1),M
0070 CLOSE FILE (0)
0080 OPEN FILE (0,3),"39.MX"
0090 MAT READ FILE (0),R,M
0100 MAT WRITE FILE (1),M
0110 CLOSE FILE (0)
0120 OPEN FILE (0,3),"45.MX"
0130 DIM M(9,37)
0140 MAT READ FILE (0),R,M
0150 MAT WRITE FILE (1),M
0160 CLOSE
0170 CHAIN "CLUSTER2"
```

dated: 14 / 10 / 1985

CLUSTER2

```
0010 !cluster2
0020 PRINT "Enter <30>D 0 <30>E for distance coefficient"
0021 PRINT "or    <30>D 1 <30>E for correlation coefficient"
0025 INPUT H
0030 DIM R(37),M(45,37),N(18,18),Z$(10),S$(80)
0040 RESTORE 1630
0070 FOR G=1 TO 6
0080   IF G-1 THEN GOTO 0390
0090   OPEN FILE (0,3),"CORE.MX"
0100   OPEN FILE (1,1),"CORE.MT"
0110   MAT READ FILE (0),M
0120   IF H THEN GOTO 0370
0130   PRINT "<12><13>results being averaged<13><13>"
0140   FOR I=1 TO 37
0150     PRINT "<13><20>";I;"<21>"
0160     LET N=0
0170     LET S=0
0180     FOR J=1 TO 45
0190       IF M(J,I)<=0 THEN GOTO 0220
0200       LET N=N+1
0210       LET S=S+M(J,I)
0220       PRINT M(J,I),
0230     NEXT J
0240     LET R(I)=0
0250     IF S THEN LET R(I)=S/N
0260     PRINT "<13>"
0270   NEXT I
0280   PRINT "Standardised format<13><13>"
0290   FOR I=1 TO 37
0300     PRINT "<13><20>";I;"<21>"
0310     FOR J=1 TO 45
0320       IF M(J,I)<>-9999 THEN IF M(J,I) THEN LET M(J,I)=M(J,I)/R(I)
0330       PRINT M(J,I),
0340     NEXT J
0350     PRINT "<13>"
0360   NEXT I
0370   MAT WRITE FILE (1),M
0380   CLOSE
0390   OPEN FILE (0,3),"CORE.MT"
0400   MAT READ FILE (0),M
0410   CLOSE
0420   READ Z$
0430   LET P=VAL(Z$(1,1))
0440   LET O$=Z$(2,6)
0450   LET I1=VAL(Z$(7,8))
0460   LET J1=VAL(Z$(9,10))
0470   LET X=0
0480   OPEN FILE (0,1),"OrdCoeff"
0490   LET N0=18
```

```
CLUSTER2cont
0510   LET N1=18
0520   IF G=6 THEN LET N1=9
0530   DIM N(N0,N1)
0540   FOR I=1 TO N0
0550     FOR J=1 TO N1
0560       LET N(I,J)=-9999
0570     NEXT J
0580   NEXT I
0590   FOR J=J1 TO N1-P-1+J1
0600     IF M(J,1)=-9999 THEN GOTO 0810
0610     LET N2=I1
0620     IF P THEN LET N2=J+1
0630     FOR I=N2 TO I1+N0-1
0640       IF M(I,1)=-9999 THEN GOTO 0800
0650       PRINT I;J,
0660       LET D=0
0670       LET S0=0 !sum xi
0680       LET S1=0 !sum xj
0690       LET S2=0 !sum xi2
0700       LET S3=0 !sum xj2
0710       LET S4=0 !sum xixj
0720       FOR K=1 TO 37
0730         IF M(I,K)=-9999 THEN GOTO 0760
0740         IF H=0 THEN LET D=D+(M(I,K)-M(J,K))↑2
0750         IF H THEN GOSUB 1260
0760       NEXT K
0770       IF H THEN GOSUB 1320
0780       IF H=0 THEN LET N(I-I1+1,J-J1+1)=INT((SQR(D/37)+.005)*100)
0790       PRINT N(I-I1+1,J-J1+1)
0800     NEXT I
0810   NEXT J
0820   IF X=0 THEN GOSUB 1370
0830   IF P=0 THEN GOTO 1220
0840   LET S=1E+06
0850   IF H THEN LET S=-1
0860   FOR J=1 TO N1-P
0870     IF P THEN LET N2=J+1
0880     FOR I=N2 TO N0
0890       IF N(I,J)=-9999 THEN GOTO 0950
0900       IF H=0 THEN IF N(I,J)>=S THEN GOTO 0950
0910       IF H THEN IF N(I,J)<S THEN GOTO 0950
0920       LET I0=I
0930       LET J0=J
0940       LET S=N(I,J)
0950     NEXT I
0960   NEXT J
0970   PRINT FILE (0),I0,J0,S
0980   LET I0=I0+I1-1
0990   LET J0=J0+J1-1
```

CLUSTER2cont

```
1010      LET M(I0,J)=(M(I0,J)+M(J0,J))/2
1020      LET M(J0,J)=-9999
1030    NEXT J
1040    LET X=0
1050    FOR I=I1 TO I1+N0-1
1060      IF M(I,1)>-9999 THEN LET X=X+1
1070    NEXT I
1080    PRINT X
1090    IF X>1 THEN GOTO 0490
1100    CLOSE FILE (0)
1110    OPEN FILE (0,3),"OrdCoeff"
1120    OPEN FILE (1,1),"$LPT"
1130    LET E=0
1140    PRINT FILE (1),"<13><27><Relative order of segment similarities for";O$;"<27>=<13>"
1150    PRINT FILE (1),"segment I      segment J      coefficient"
1160    PRINT FILE (1),"=========      =========      ==========="
1170    INPUT FILE (0),S$
1180    IF EOF(0) THEN GOTO 1210
1190    PRINT FILE (1),S$
1200    GOTO 1170
1210    PRINT FILE (1),"<13>";SYS(1);"/";SYS(2);"/";SYS(3)-1900
1220    CLOSE
1230  NEXT G
1240  PRINT "Restart by <30>D RUN <30>E<7>"
1250  STOP
1260  LET S0=S0+M(I,K)
1270  LET S1=S1+M(J,K)
1280  LET S2=S2+M(I,K)*M(I,K)
1290  LET S3=S3+M(J,K)*M(J,K)
1300  LET S4=S4+M(I,K)*M(J,K)
1310  RETURN
1320  LET R=(S4-S0*S1/37)/SQR((S2-S0*S0/37)*(S3-S1*S1/37))
1330  IF R>0 THEN LET R=R+.0005
1340  IF R<0 THEN LET R=R-.0005
1350  LET N(I-I1+1,J-J1+1)=INT(R*1000)/1000
1360  RETURN
1370  OPEN FILE (1,1),"$LPT"
1380  TAB =6
1390  PRINT FILE (1),"<13><27><Distance coefficient down ";O$;"<27>="
1400  PRINT FILE (1),,
1410  FOR I=1 TO N1
1420    PRINT FILE (1),STR$(I),
1430  NEXT I
1440  PRINT FILE (1)
1450  FOR I=1 TO N1+1
1460    PRINT FILE (1),"==",
1470  NEXT I
1480  PRINT FILE (1)
1490  FOR I=1 TO N0
```

CLUSTER2cont

```
1510    IF I>9 THEN LET I$=I$(2)
1520    PRINT FILE (1),I$;" |",
1530    FOR J=1 TO N1
1540      IF N(I,J)>=0 THEN PRINT FILE (1),STR$(N(I,J)),
1550      IF N(I,J)<0 THEN PRINT FILE (1),"  ",
1560    NEXT J
1570    PRINT FILE (1)
1580 NEXT I
1581 IF P=0 THEN PRINT FILE (1), TAB(60);"<27><core ";O$(4,5);" across page<27>="
1582 IF P=0 THEN PRINT FILE (1), TAB(60);"<27><core ";O$(1,2);" down page<27>="
1590 PRINT FILE (1),"<13><13>";SYS(1);"/";SYS(2);"/";SYS(3)-1900
1600 CLOSE FILE (1)
1610 TAB =14
1620 RETURN
1630 DATA "114-140101","139-391919","039-141901","045-143701","045-393719","145-453737"
```

dated: 14 / 10 / 1985

TABLE E.3. "KINETICPLOT" and "PLOTDATA" computer programs for reaction order fit to data of Kinetic Rate experiments.

```
KINETICPLOT
0010 !KINETICPLOT
0020 DIM A(100,3) !limited to 100 data pairs
0030 DIM H$(132),M$(132),L(3),U$(80),U(3),V(3)
0040 PRINT "<12><13><30>D This program takes data pairs and carries out least squares correlation"
0050 PRINT "to fit 1st, 2nd, 3rd order kinetics and part-order tests over selected"
0060 PRINT "x-axis ranges for plots<30>E<13>"
0070 OPEN FILE (0,2),"2bplotted"
0080 GPOS FILE (0),L
0090 CLOSE
0100 IF L=0 THEN GOTO 0160
0110 PRINT "There are";L;" bytes on file waiting to be plotted"
0120 INPUT "Do you wish to DELETE these ?<7> ",O$
0130 IF O$="N" THEN GOTO 0160
0140 IF O$<>"Y" THEN GOTO 0120
0150 DELETE "2BPLOTTED"
0160 LREAD "Enter title of graph (must have determinand name and conditions)<13>? ",H$
0170 ON ERR THEN RETRY
0180 PRINT "Enter units for x-axis (time):"
0190 INPUT "0 for secs, 1 for mins, 2 for hrs, 3 for days ? ",O
0200 IF O<>ABS(INT(O)) THEN GOTO 0190
0210 IF O>3 THEN GOTO 0190
0220 IF O=0 THEN LET X1=1
0230 IF O=1 THEN LET X1=-1.66667E-02
0240 IF O=2 THEN LET X1=2.77778E-04
0250 IF O=3 THEN LET X1=1.15741E-05
0260 PRINT "Enter units for y-axis (concentration):"
0270 INPUT "0 for mM/l, 1 for mg/l ? ",Y1
0280 IF Y1<>0 THEN IF Y1<>1 THEN GOTO 0270
0290 IF Y1 THEN INPUT "Enter M.W. ? ",Y1
0300 IF Y1 THEN IF Y1<10 THEN GOTO 0260
0310 IF Y1>100 THEN GOTO 0260
0320 ON ERR THEN STOP
0330 IF O=0 THEN LET X$="s"
0340 IF O=1 THEN LET X$="min"
0350 IF O=2 THEN LET X$="hr"
0360 IF O=3 THEN LET X$="day"
0370 IF Y1=0 THEN LET Y$="mM"
0380 IF Y1 THEN LET Y$="mg/l"
0390 PRINT "<13>Data will be considered for fit over up to 3 bands for independent variable (X)"
0400 GOSUB 1800
0410 PRINT "for example 0,100,5 will give a lower limit of 0 and an upper limit of 500"
0420 PRINT "(e.g. 0-1 hr, 0-500 hr, 1-500 hr)"
0430 LET P=3
0440 FOR I=1 TO 3
0450   PRINT "BAND ";I;
0460   INPUT ". Enter lower limit, interval, no.intervals (0,0,0 to finish)<13>? ",L(I),U(I),V(I)
0470   IF L(I) THEN IF U(I)=0 THEN GOTO 0720
0480   IF L(I) THEN IF V(I)=0 THEN GOTO 0720
0490   IF V(I) THEN IF ABS(INT(V(I)-3))<>V(I)-3 THEN GOTO 0720
```

KINETICPLOTcont

```
0510    IF V(I)=0 THEN LET P=I-1
0520    IF V(I)=0 THEN LET I=3
0530    LET U(I)=U(I)*V(I)+L(I)
0540  NEXT I
0550  FOR I=1 TO 100
0560    INPUT "Enter data in pairs (X,Y) (0,0 to finish) ? ",A(I,1),A(I,2)
0570    IF A(I,1)=0 THEN IF A(I,2)=0 THEN LET N=I-1
0580    IF A(I,1)=0 THEN IF A(I,2)=0 THEN LET I=100
0590  NEXT I
0600  PRINT "CHECK DATA:-<13>PAIR NO."; TAB(20);"X"; TAB(40);"Y"
0610  FOR I=1 TO N
0620    PRINT I; TAB(20);A(I,1); TAB(40);A(I,2)
0630  NEXT I
0640  INPUT "IS DATA CORRECT ? ",O$
0650  IF O$="Y" THEN GOTO 0740
0660  IF O$="" THEN GOTO 0740
0670  IF O$<>"N" THEN GOTO 0640
0680  INPUT "ENTER PAIR NO.,X,Y TO CORRECT ? ",I,X,Y
0690  LET A(I,1)=X
0700  LET A(I,2)=Y
0710  GOTO 0600
0720  PRINT "INCORRECT ENTRY"
0730  GOTO 0450
0740  FOR K=0 TO 4 !order
0750    FOR I=1 TO N
0760      IF K=0 THEN LET A(I,3)=A(I,2)
0770      IF K=1 THEN LET A(I,3)=LOG(A(I,2)) ! log base e
0780      IF K=2 THEN LET A(I,3)=1/A(I,2)
0790      IF K=3 THEN LET A(I,3)=1/(A(I,2)*A(I,2))
0800      IF K=4 THEN IF I>1 THEN LET A(I,3)=A(I,1)/(1-A(I,2)/A(1,2))
0810    NEXT I
0820    FOR J=1 TO P !band
0830      LET L=-1
0840      LET U=-1
0850      FOR I=1 TO N
0860        IF L=-1 THEN IF VAL(STR$(A(I,1)))>=VAL(STR$(L(J))) THEN LET L=I
0870        IF U=-1 THEN IF VAL(STR$(A(I,1)))=VAL(STR$(U(J))) THEN LET U=I
0880        IF U=-1 THEN IF VAL(STR$(A(I,1)))>VAL(STR$(U(J))) THEN LET U=I-1
0890      NEXT I
0900      IF U=-1 THEN LET U=N
0910      LET X=0
0920      LET Y=0
0930      FOR I=L TO U
0940        LET X=X+A(I,1)
0950        LET Y=Y+A(I,3)
0960      NEXT I
0970      LET X=X/(U-L+1) !mean x
0980      LET Y=Y/(U-L+1) !mean y
0990      LET A=0
1000      LET B=0
```

KINETICPLOTcont

```
1010      LET D=0
1020      LET E=0
1030      LET F=0
1040      LET Z1=A(1,3)
1050      LET Z2=Z1
1060      FOR I=L TO U
1070        LET A=A+(A(I,1)-X)↑2 !                    <X↑2
1080        LET B=B+(A(I,1)-X)*(A(I,3)-Y) !           <XY
1090        LET D=D+(A(I,3)-Y)↑2 !                    <Y↑2
1100        LET E=E+A(I,1) !                          <x
1110        LET F=F+A(I,3) !                          <y
1120        IF A(I,3)<Z1 THEN LET Z1=A(I,3)
1130        IF A(I,3)>Z2 THEN LET Z2=A(I,3)
1140      NEXT I
1150      LET M=B/A
1160      LET C=(A*F-E*B)/((U-L+1)*A)
1170      LET R=B/SQR(A*D)
1180      IF K THEN IF R<.95 THEN PRINT "For band";J;" order";K;" corr.coeff.=";R;" & is not being plotted"
1190      IF K THEN IF R<.95 THEN GOTO 1630
1200      OPEN FILE (0,2),"2BPLOTTED"
1210      PRINT FILE (0),"!";H$
1220      IF K=0 THEN PRINT FILE (0),"!Depletion study"
1230      IF K=0 THEN LET O$=""
1240      IF K=4 THEN LET O$=""
1250      IF K=1 THEN LET O$="First"
1260      IF K=2 THEN LET O$="Second"
1270      IF K=3 THEN LET O$="Third"
1280      IF K=4 THEN PRINT FILE (0),"!Kinetic fit after Wilkinson"
1290      IF K THEN IF K<4 THEN PRINT FILE (0),"!Fit for ";O$;" Order Kinetics" !vitally important not to alter O$ statements
1300      IF K=0 THEN LET U$=Y$
1310      IF K=1 THEN LET U$="ln(",Y$,")"
1320      IF K=2 THEN LET U$="1/(",Y$,")"
1330      IF K=3 THEN LET U$="1/(",Y$,")**2"
1340      IF K=4 THEN LET U$=X$,"/(1-fract.reacted)"
1350      LET K0=M*X1
1360      IF K=1 THEN IF Y1 THEN LET K0=K0/LOG(Y1)
1370      IF K=2 THEN IF Y1 THEN LET K0=K0*Y1
1380      IF K=3 THEN IF Y1 THEN LET K0=K0*Y1*Y1
1390      PRINT FILE (0),X$;",";U$
1400      PRINT FILE (0),STR$(L(J));",";STR$((U(J)-L(J))/V(J));":";STR$(V(J))
1410      PRINT "<12><13><30>D For ";H$;"<13><30>E";O$
1420      PRINT "For y-axis range is";Z1;" to";Z2
1430      GOSUB 1800
1440      INPUT "Enter lower limit, interval, no.intervals ? ",Z3,Z4,Z5
1450      IF Z1<Z3 THEN GOTO 1830
1460      IF Z2>Z3+Z4*Z5 THEN GOTO 1830
1470      LET Q=70/(Z4*Z5)
1480      PRINT  TAB(5);"!"; TAB(INT(Q*(Z1-Z3)+5));"<30>D data range"; TAB(INT(Q*(Z2-Z3)+5));"<30>E"; TAB(75);"!"
1490      PRINT  TAB(5);Z3; TAB(70);Z3+Z4*Z5
```

KINETICPLOTcont

```
1510      IF O$="N" THEN GOTO 1440
1520      IF O$<>"Y" THEN IF O$<>"" THEN GOTO 1500
1530      PRINT FILE (0),STR$(Z3);",";STR$(Z4);":";STR$(Z5)
1540      FOR I=L TO U
1550        IF I=1 THEN IF K=4 THEN GOTO 1570
1560        PRINT FILE (0),STR$(A(I,1));",";STR$(A(I,3))
1570      NEXT I
1580      PRINT FILE (0),"-1,-1"
1590      IF K THEN LET M$="C",STR$(C),"M",STR$(M),"R",STR$(R),"K",STR$(K0)
1600      IF K THEN PRINT FILE (0),M$;"I";STR$(A(1,2));"J";STR$(X1);"L";STR$(Y1)
1610      IF K=0 THEN PRINT FILE (0),"*"
1620      CLOSE FILE (0)
1630    NEXT J
1640 NEXT K
1650 CLOSE
1660 INPUT "More data ? ",Y$
1670 IF Y$="Y" THEN GOTO 0160
1680 IF Y$<>"N" THEN GOTO 1660
1690 INPUT "Enter DELETE to delete back up copy of data to be plottted ? ",Y$
1700 LET I=2
1710 IF Y$="DELETE" THEN LET I=1
1720 OPEN FILE (0,3),"2BPLOTTED"
1730 OPEN FILE (1,I),"FULLPLOT.CY"
1740 LREAD FILE (0),H$
1750 IF EOF(0) THEN GOTO 1780
1760 PRINT FILE (1),H$
1770 GOTO 1740
1780 CLOSE
1790 CHAIN "PLOTOUT"
1800 PRINT "You will need to enter lower limit and sensible interval bearing in mind that"
1810 PRINT "between 3 and 5 intervals may be included on the plot"
1820 RETURN
1830 PRINT "<7>Range will not fit within the graph"
1840 GOTO 1440
```

dated: 14 / 10 / 1985

PLOTDATA

```
0010 !PLOTOUT FOR KINETICS PLOTS
0020 DIM A$(80),H$(80),O$(80),T$(80),T1$(80),U$(80),X0$(20),Y0$(20)
0030 GOTO 1130
0040 OPEN FILE (2,3),"2BPLOTTED"
0050 LREAD FILE (2),H$
0060 IF EOF(2) THEN GOTO 1160
0070 OPEN FILE (1,1),"QTY:3"
0080 LET A$=";: I OD 100 H"
0090 GOSUB 1180
0100 LET A$="R 400,500 0 A"
0110 GOSUB 1180
0120 LREAD FILE (2),O$
0130 LREAD FILE (2),U$
0140 LREAD FILE (2),X0$
0150 LREAD FILE (2),Y0$
0160 LET X=VAL(X0$) !lower limit x axis
0170 LET X1=VAL(X0$(POS(X0$,",",2)+1)) !interval x axis
0180 LET X6=VAL(X0$(POS(X0$,":",2)+1)) !no. of intervals
0190 LET X0=INT(2100/X6) ! size of interval in .1mm
0200 LET Y=VAL(Y0$)
0210 LET Y1=VAL(Y0$(POS(Y0$,",",2)+1))
0220 LET Y6=VAL(Y0$(POS(Y0$,":",2)+1))
0230 LET Y0=INT(1400/Y6)
0240 LET A$="D"
0250 GOSUB 1180
0260 FOR I=Y0 TO Y0*Y6 STEP Y0
0270   LET A$="0,",STR$(I)," M11"
0280   IF I=Y0*Y6 THEN LET A$=A$," U"
0290   GOSUB 1180
0300 NEXT I
0310 LET A$="200,1510 S12 ",H$(2)," _ 200,1450"
0320 GOSUB 1180
0330 LET A$="S12 ",O$(2)," _"
0340 GOSUB 1180
0350 FOR I=Y0*Y6 TO 0 STEP -Y0
0360   LET Y2=Y+I*Y1/Y0
0370   LET L=LEN(STR$(Y2))
0380   LET A$=STR$(INT(-L*25-40)),",",STR$(I-20)," S12 ",STR$(Y2)," _"
0390   GOSUB 1180
0400   IF I=3*Y0 THEN GOSUB 1510
0410 NEXT I
0420 LET A$="0,0 D"
0430 GOSUB 1180
0440 FOR I=X0 TO X0*X6 STEP X0
0450   LET A$=STR$(I),",0 M11"
0460   IF I=X0*X6 THEN LET A$=A$," U"
0470   GOSUB 1180
0480 NEXT I
0490 LET A$="1750,-120 S12 DATED:",STR$(SYS(1)),"/",STR$(SYS(2)),"/",STR$(SYS(3)-1900),"
0500 GOSUB 1180
```

PLOTDATAcont

```
0510 FOR I=X0*X6 TO 0 STEP -X0
0520   LET X2=X+I*X1/X0
0530   LET L=LEN(STR$(X2))
0540   LET A$=STR$(I-L*12),",-60 S12 ",STR$(X2)," _"
0550   GOSUB 1180
0560   IF I=3*X0 THEN GOSUB 1560
0570 NEXT I
0580 LREAD FILE (2),U$
0590 IF U$="-1,-1" THEN GOTO 0670
0600 LET X3=INT((VAL(U$)-X)*X0/X1)
0610 LET Y3=INT((VAL(U$(POS(U$,",",1)+1))-Y)*Y0/Y1)
0620 LET U$=STR$(X3),",",STR$(Y3)
0630 LET A$=U$," D M11"
0640 IF O$(2,2)<>"D" THEN LET A$=A$," U"
0650 GOSUB 1180
0660 GOTO 0580
0670 LET T$=""
0680 LET T1$=""
0690 LREAD FILE (2),U$
0700 IF U$="*" THEN GOTO 0950
0710 LET T1$="S12 s _ R 0,30 S12 -1 _ A"
0720 IF O$(10,10)="F" THEN LET T$=T1$
0730 IF O$(10,10)="S" THEN GOSUB 1210
0740 IF O$(10,10)="T" THEN GOSUB 1220
0750 LET J=80
0760 IF O$(10,10)="F" THEN LET J=1200
0770 IF O$(10,10)="F" THEN LET I=-1
0780 LET C=VAL(U$(2))
0790 LET M=VAL(U$(POS(U$,"M",1)+1))
0800 LET R=VAL(U$(POS(U$,"R",1)+1))
0810 LET K0=VAL(U$(POS(U$,"K",1)+1))
0820 LET A$="P2"
0830 GOSUB 1180
0840 GOSUB 1250
0850 IF O$(2,2)="K" THEN GOSUB 1390
0860 GOSUB 1230
0870 LET A$="1200,",STR$(J)," S12 Rate Constant (k) ",STR$(K0)," _ ",T$
0880 GOSUB 1180
0890 IF O$(10,10)="F" THEN GOTO 0920
0900 LET A$=T1$
0910 GOSUB 1180
0920 LET A$="1100,",STR$(J+70)," S12 Correlation Coeff.(r) ",STR$(R)," _"
0930 GOSUB 1180
0940 GOTO 0970
0950 LET A$="U"
0960 GOSUB 1180
0970 LET A$="PO Z @"
0980 GOSUB 1180
0990 CLOSE FILE (1)
1000 GPOS FILE (2),L
```

```
PLOTDATA:cont
1010 OPEN FILE (0,1),"NEXTPLOT"
1020 SPOS FILE (2),L
1030 LREAD FILE (2),H$
1040 IF EOF(2) THEN GOTO 1070
1050 PRINT FILE (0),H$
1060 GOTO 1030
1070 CLOSE
1080 ON ERR THEN GOTO 1100
1090 DELETE "2BPLOTTED.CY"
1100 ON ERR THEN STOP
1110 RENAME "2BPLOTTED","2BPLOTTED.CY"
1120 RENAME "NEXTPLOT","2BPLOTTED"
1130 INPUT "TYPE OK IF PLOTTER SET READY TO START ? ",O$
1140 IF O$<>"OK" THEN STOP
1150 GOTO 0040
1160 CLOSE
1170 STOP
1180 PRINT FILE (1),A$
1190 INPUT FILE (1),Z$
1200 RETURN
1210 LET I=1
1220 IF O$(10,10)="T" THEN LET I=2
1230 LET T$="S12 M _ R 0,30 S12 -",STR$(I)," _ 0,-30 A "
1240 RETURN
1250 LET I0=M*X+C
1260 LET I1=M*(X+X1*X6)+C
1270 LET I2=(Y-C)/M
1280 LET I3=(Y-C+Y1*Y6)/M
1290 LET O$=""
1300 IF I0>Y THEN IF I0<Y+Y1*Y6 THEN LET O$="!0,",STR$(INT((I0-Y)*Y0/Y1))
1310 IF I1>Y THEN IF I1<Y+Y1*Y6 THEN LET O$=O$,"!",STR$(X0*X6),",",STR$(INT((I1-Y)*Y0/Y1))
1320 IF I2>X THEN IF I2<X+X1*X6 THEN LET O$=O$,"!",STR$(INT((I2-X)*X0/X1)),",0"
1330 IF I3>X THEN IF I3<X+X1*X6 THEN LET O$=O$,"!",STR$(INT((I3-X)*X0/X1)),",",STR$(Y0*Y6)
1340 IF O$="" THEN STOP
1350 LET P=POS(O$,"!",3)
1360 LET A$=O$(2,P-1)," D ",O$(P+1)," U"
1370 GOSUB 1180
1380 RETURN
1390 LET K1=INT(2*M*100)/100
1400 LET A$="1390,10 S12 Order      ",STR$(K1)," _ "
1410 GOSUB 1180
1420 LET C0=VAL(U$(POS(U$,"I",1)+1))
1430 LET X7=VAL(U$(POS(U$,"J",1)+1))
1440 LET Y7=VAL(U$(POS(U$,"L",1)+1))
1450 LET K0=1/C
1460 LET K0=K0/C0↑(K1-1)
1470 LET K0=K0*X7*Y7↑(K1-1)
1480 LET I=K1-1
1490 LET J=80
1500 RETURN
```

PLOTDATAcont

```
1510 LET A$="-160,",STR$(2*Y0+20),"  D"
1520 GOSUB 1180
1530 LET A$="S42 ",U$(POS(U$,",",1)+1),"  _  "
1540 GOSUB 1180
1550 RETURN
1560 LET A$=STR$(X0*2.25),",-120 S12 ",U$(1,POS(U$,",",1)-1),"  _  "
1570 GOSUB 1180
1580 RETURN
```

dated: 14 / 10 / 1985

TABLE E.4. "WATDEPOSIT" and "ITERATE" computer programs forming the model WATDEPOSIT as used for calculating the speciation of determinands generated by the mixing of inlets and including equilibrium deposition of mineral phases.

```
WATDEPOSIT
0010 !WATDEPOSIT
0020 DIM L$(20),H$(20),M$(20),O$(65)
0030 PRINT "<12><13><30>D Press ESC to reconsider input <30>E"
0040 ON ESC THEN GOTO 6960
0050 PRINT "<13>WATDEPOSIT. This program takes total dissolved determinand results from two"
0060 PRINT "stations discharging into a water body and identifies speciation of those"
0070 PRINT "determinands in each constituent water and the mixed body. It also indicates"
0080 PRINT "which minerals can be formed and will quantify these. It then generates a"
0090 PRINT "post-deposition speciation<13>"
0100 PRINT "Enter title of station with lowest flow"
0110 PRINT  TAB(20);"]<13><23>";
0120 LREAD "[",L$
0130 OPEN FILE (0,1),"Mixtitles",66
0140 PRINT FILE (0),L$
0150 PRINT "Enter title of other station"
0160 PRINT  TAB(20);"]<13><23>";
0170 LREAD "[",H$
0180 PRINT FILE (0),H$
0190 PRINT "Enter title of mixed water body"
0200 PRINT  TAB(55-LEN(L$)-LEN(H$));"]<13><23>";
0210 LREAD "[",M$
0220 PRINT "<13>Now enter flow data :<13>--- ----- ---- ----"
0230 PRINT "FOR SINGLE FLOW RATIO. When asked enter lower flow <34>,<34> higher flow <34>,0<34>."
0240 PRINT "FOR SEVERAL FLOW RATIOS. Enter in one or more groups. Each group of ratios"
0250 PRINT "  should start at a minimum ratio and proceed via a regular interval to a"
0260 PRINT "  maximum ratio. The lower-flow-water is taken as unity. For instance "
0270 PRINT "  10,50,5 will investigate 1:10,1:15,etc to 1:50 ratios of ";L$;" to ";H$;". Finish with 0,0,0"
0275 PRINT " ?min.?max.?int.<13>  ===  ===  ==="
0280 LET O$=" ",L$,":",H$,")"
0290 INPUT L,H,V
0300 IF L THEN IF V=0 THEN GOTO 0360
0310 IF L=0 THEN GOTO 0370
0320 FOR I=L TO H STEP V
0330   PRINT FILE (0),M$;" (1:";STR$(I);O$
0340 NEXT I
0350 GOTO 0290
0360 PRINT FILE (0),M$;" (";STR$(L);":";STR$(H);O$
0370 CLOSE
0380 PRINT "<13>Proposed headings are as follows - press ESC if not correct"
0385 PRINT "======== ======== === == ======="
0390 OPEN FILE (0,3),"Mixtitles",66
0400 LREAD FILE (0),O$
0410 IF EOF(0) THEN GOTO 0460
0420 PRINT O$
0430 DELAY =1
0440 GOTO 0400
0450 ON ESC THEN STOP
0460 CLOSE
0470 INPUT "<13><7>Enter<30>D temperature        <30>Eof mixed water body C       ? ",T
0480 ON ESC THEN GOTO 0450
```

```
WATDEPOSIT.con't
0490 INPUT "Enter<30>D dissolved oxygen  <30>Eof mixed water body mg/l O ? ",O
0495 LET O=O/32000
0496 LET T1=T+273.2
0497 LET A9=.48863+T*7.48*10↑-4+T*T*3.85*10↑-6 !D-H equation det A
0498 LET B9=.32415+T*1.65*10↑-4+T*T*2*10↑-7 !D-H B
0510 OPEN FILE (0,1),"Constants"
0515 WRITE FILE (0),T,O,A9,B9
0520 PRINT "<13>Now enter analysis of ";L$
0530 GOSUB 7000
0540 PRINT "Now enter analysis of ";H$
0550 GOSUB 7000
0600 DIM K(77),K2(77),K3(40)
0610 RESTORE 0620
0620 DATA 8,9,19,22,26,27,28,29,30,31,33,36,40,41,42,43,45,46,47,48,49,50,51,53,54,55,56,57,58,59,60
0630 DATA 61,63,65,66,73,74,75,76
0640 MAT READ I1(39)
0650 DATA 6,20,21,23,24,25,32,35,37,38,44,62,64,68,77
0660 MAT READ I2(15)
0670 DATA -33.938,26.571,-1.4,-2.309,-2.238,1.602,-1.268,.25,-.72,1.585,6.1,1,-8.998,-18.235,-3.2,-5.1,13.013,11.6
0680 DATA 11.925,15.473,20.173,34.894,8.886,10.919,9.319,20.57,29.458,-2.2,-.82,-.64,-.2,-.64,12.918,-1.11,21.495
0690 DATA 13.998,-40.644,-30.741,-119.077,8.215,4.548,8.24,-1.582,11.41,5.974,9.756,13.32,10.55,.179,11.41,32.77
0700 DATA 3.523,4.005,17.02,4.759,5.211,1.113,4.631,30.51,41.2,33.41,-24.15,18,63.53,20.57,49.09,19.33,62.29,36.91
0710 DATA 32.82,90.61,42.43,37.82,-32.67,18.48,17.97,40.31,45
0720 MAT READ K1(78)
0730 DATA -9.32,0,1.19,1.5,1.27,0,8.911,0,1.1,0,18.63,10,1.99,0,2.29,3.07,9.7,18.152,0,20.115,0,0,15.92,0,13.218
0740 DATA 28.565,32.995,.56,1.15,1.75,4.832,0,12.1,0,33.457,13.345,-65.44,-57.435,-187.055,-2.959,-3.769,-6.169
0750 DATA .918,2.361,-1.054,6.141,6.95,-5.328,-.572,.85,14.47,4.615,6.22,-8.29,.261,-4.551,18.987,0,-25.76,25.555
0760 DATA 11.905,-49.65,25.896,0,30.82,67.86,17.53,45.065,49.15,44.68,54.76,0,-25.52,-68.86,11.3,0,54.684,58.373
0770 MAT READ H1(78)
0780 DATA -6.498,-27.393,-2.95,.684,.991,2.319,3.106,-5.3505,6.368,39.478,28.6059,11.17,.6322,-14.8435,-14.0184
0790 MAT READ A1(15)
0800 DATA .02379,.05617,.01333,5.1295E-03,.00667,-.011056,0,1.83412E-02
0810 DATA -.016346,-.065927,-.012078,-.02386,-.001225,.032786,.015264
0820 MAT READ A2(15)
0830 DATA 2902.39,4114,0,0,0,0,-673.6,557.25,-3405.9,-12355.1,1573.21,-3279,-2835.76,3404.71,2385.73
0840 MAT READ A3(15)
0850 FOR I=1 TO 39
0860   LET K2(I1(I))=K1(I)+H1(I)*(25-T)/(T1*1.36424)
0870   IF I1(I)<>76 THEN LET K(I1(I))=10↑(-K2(I1(I)))
0880 NEXT I
0890 FOR I=1 TO 15
0900   LET K2(I2(I))=-A1(I)-A2(I)*T1-A3(I)/T1
0910   IF I=6 THEN LET K2(I2(I))=K2(I2(I))-2.29812*10↑(-5)*T1*T1
0920   IF I=11 THEN LET K2(I2(I))=K2(I2(I))+5.74386*LOG(T1)+K2(73)
0930   LET K(I2(I))=10↑-K2(I2(I))
0940 NEXT I
0950 FOR I=1 TO 39
0960   LET K3(I+1)=K1(I+39)+H1(I+39)*(25-T)/(T1*1.36424)
0970 NEXT I
0980 LET K3(1)=-13.543+.0401*T1+3000/T1
```

WATDEPOSIT con't

```
0990 LET K3(17)=4.6535-T*(.004545-.000101*T)
1000 LET K3(20)=K3(20)-K(73)
1010 LET K3(24)=K3(24)-6*K(73)-2*K(45)
1020 LET K3(36)=K3(36)-8*K(73)-2*K(45)
1030 LET K3(37)=K3(37)-4*K(73)-2*K(45)
1040 LET K3(38)=K3(38)-4*K(73)-2*K(45)
1050 LET 0=0/32000
1055 RESTORE 1060
1060 DATA 19,20,21,22,23,24,25,26,27,28,29,30,31,32,33,35,58,59,60,61,68
1070 MAT READ P(21)
1080 DATA 1,1,1,1,2,2,2,2,3,3,3,3,4,4,71,71,10,11,12,12,71
1090 DATA 72,34,6,7,72,34,6,7,5,34,6,7,5,7,5,7,72,72,72,7,6
1100 MAT READ I3(21,2)
1110 DATA 2,2,1,1,-1,-1,-2,-1,0,2,2,1,-1,0,0,-1,0,1,1,0,1,0,1,0,1,0,0,-1,0,-1,0,-1,0,-2,-1,0,-1
1120 DATA -2,3,2,1,1,-1,-1,3,2,0,2,1,-1,1,2,1,1,0,-1,0,1,1,0,-1,-1,-2,0,-1,0,0,0,0,0,1,-1
1130 MAT READ C(72)
1140 DATA 5,5.5,4,3.5,3.5,5.4,5,4.5,0,5,5,6,3,0,2.5,4,0,0,6,0,6,0,6.5,0,4,0,0,5.4,0,5.4,0,5.4,0,5.4,4.5,0,4
1150 DATA 5.4,9,5.4,5.4,4.5,4.5,0,9,5,0,5,5.4,5.4,5,6,5,5,0,5,0,5,5,0,5,3.5,5,0,5,0,0,0,0,0,9,3.5
1160 MAT READ R(72)
1170 DATA 1,1,1,1,0,0,0,0,0,1,0,1,1,1,1,2,1,1,0,1,4,1,1,2,1,1,1,1,1,3,2,2,5,2,3,1,2,2,.6,.17
1180 DATA 1,1,1,1,0,0,0,0,0,1,0,2,3,0,0,1,1,1,0,1,1,3,3,6,1,6,1,2,2,6,2,2,2,2,2,8,4,4,1.2,2
1190 DATA 0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,1,0,0,0,1,3,0,0,0,3,1,3,3,2,4,2,2,3,4,4,2,2,4,2.3,3.67
1200 DATA 0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,3,0,3,0,0,0,0,8,0,0,0,-1,1,3.5,2.33
1210 MAT READ N1(40,4)
1220 DATA 34,34,1,34,0,0,0,0,0,34,0,2,39,14,14,34,1,34,0,52,34,45,39,45,3,4,4,4,1,2,8,8,2,8,34,52,62,45,4,1
1230 DATA 1,1,7,2,0,0,0,0,0,52,0,72,72,0,0,2,7,2,0,72,1,72,72,72,8,72,8,71,8,72,71,71,72,71,72,72,72,72,71,71
1240 DATA 0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,1,0,0,0,62,2,0,0,0,14,8,14,14,14,14,14,14,14,14,2,45,45,62,8,14
1250 DATA 0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,14,0,8,0,0,0,0,8,0,0,0,52,52,14,8
1260 MAT READ S1(40,4)
1270 DATA .165,.2,.075,.015,.015,0,-.04
1275 MAT READ B(7)
1280 DATA 1,2,3,4,12,13,16,17,18,21,23,35 !Base mins taken in depn order
1285 MAT READ M(12)
1286 DATA 1,1,1,1,1,1,2,1,2,1,8,1,1,1,1,1,2,1,2,3,8,1,2,4
1287 MAT READ N0(12,2) !key dets for mins,stoich no.
1290 MAT WRITE FILE (0),K,K3,P,I3,C,R,N1,S1,B,M,N0
1300 CLOSE
1310 RESTORE 1320
1320 DATA "Ca++","Mg++","Na+","K+","Cl-","HCO3-","SO4--","Al(OH)4-","Fe(OH)3","","","","NO3-","H4SiO4","H3BO3"
1330 DATA "","H2S","NH4+","CaOH+","CaCO3","CaHCO3+","CaSO4","MgOH+","MgCO3","MgHCO3+","MgSO4","NaCl","NaCO3-","NaHCO3","NaSO4-"
1340 DATA "KCl","KSO4-","HCl","CO3--","HSO4-","H2SO4","H3SiO4-","H2SiO4--","Al+++","AlOH++","Al(OH)2+","AlSO4+"
1350 DATA "Al(SO4)2-","H2BO3-","Fe+++","FeCl++","FeCl3","FeOH++","Fe(OH)2+","Fe(OH)4-","FeSO4+","Fe++","FeCl2+"
1360 DATA "FeOH+","Fe(OH)2","FeOOH-","FeSO4","","","","","HS-","S--","NH3","NH4SO4-","O2","","H2CO3","","","H+","OH-"
1370 DATA "calcite","aragonite","anhydrite","magnesite","","","","","","siderite","","brucite","gibbsite"
1380 DATA "chalcedony","quartz","dolomite","gypsum","nesquehonite","","mackinawite","huntite","goethite","boehmite"
1390 DATA "haematite","albite","phlogopite","adularia","muscovite","anorthite","talc","kaolinite","halloysite"
1400 DATA "chlorite","pyrophyllite","hydromagnesite","magnetite","pyrite","greigite","illite","montmorillonite"
1410 DATA "calcium","magnesium","sodium","potassium","chloride"
1420 DATA "alkalinity(asHCO3)","sulphate","aluminium","iron","","","","nitrate"
1430 DATA "silica","boron","","","ammonia"
```

WATDEPOSIT cont

```
1440 OPEN FILE (0,1),"SPECMINZ"
1450 FOR I=1 TO 130
1460   READ O$
1470   WRITE FILE (0),O$
1480 NEXT I
1485 IF O$<>"ammonia" THEN STOP !error
1490 CLOSE
1500 CHAIN "ITERATE"
6960 CLOSE
6970 ON ESC THEN STOP
6980 INPUT "Type return to restart ? ",O$
6990 GOTO 0010
7000 MAT Z=ZER(18)
7010 PRINT "<13>Enter result for dissolved determinand"
7020 PRINT "===== ====== === ========= ===========<13>"
7030 INPUT "Enter <30>D pH          <30>E           ? ",H
7040 INPUT "      <30>D calcium     <30>E mg/l Ca   ? ",Z(1)
7050 INPUT "      <30>D magnesium   <30>E mg/l Mg   ? ",Z(2)
7060 INPUT "      <30>D sodium      <30>E mg/l Na   ? ",Z(3)
7070 INPUT "      <30>D potassium   <30>E mg/l K    ? ",Z(4)
7080 INPUT "      <30>D aluminium   <30>E mg/l Al   ? ",Z(8)
7090 INPUT "      <30>D iron        <30>E mg/l Fe   ? ",Z(9)
7100 INPUT "      <30>D alkalinity  <30>E mg/l CaCO3 ? ",Z(6)
7110 INPUT "      <30>D chloride    <30>E mg/l Cl   ? ",Z(5)
7120 INPUT "      <30>D sulphate    <30>E mg/l SO4  ? ",Z(7)
7130 INPUT "      <30>D silica      <30>E mg/l SiO2 ? ",Z(14)
7140 INPUT "      <30>D boron       <30>E mg/l B    ? ",Z(15)
7150 INPUT "      <30>D nitrate     <30>E mg/l N    ? ",Z(13)
7160 INPUT "      <30>D ammonia     <30>E mg/l N    ? ",Z(18)
7170 INPUT "<13> Enter <30>D Return <30>E if input is correct ? ",O$
7180 IF O$<>"" THEN PRINT "RE-ENTER THIS STATION"
7190 IF O$<>"" THEN GOTO 7000
7200 RESTORE 7210
7210 DATA 40080,24312,22990,39102,35453,50044,96062,26981,55847,1,1,1,14010,60085,10811,1,1,14010
7220 MAT READ M(18)
7230 FOR J=1 TO 18
7240   IF M(J)=1 THEN GOTO 7260
7250   LET Z(J)=Z(J)/M(J)
7260 NEXT J
7265 WRITE FILE (0),H
7270 MAT WRITE FILE (0),Z
7280 RETURN
```

dated: 14 / 10 / 1985

```
ITERATE
0010 !ITERATE
0020 !
0030 !**INPUT**
0040 !
0050 DEF FNL(X)=.434294*LOG(X)
0060 OPEN FILE (0,3),"Constants"
0070 READ FILE (0),T,O,A9,B9,H0
0080 MAT READ FILE (0),D0(18)
0090 READ FILE (0),H1
0100 MAT READ FILE (0),D1(18),K(77),K3(40),P(21),I1(21),I2(21),C(72),R(72)
0110 MAT READ FILE (0),N1(40),N2(40),N3(40),N4(40),S1(40),S2(40),S3(40),S4(40),B(7),M(12),N(12,2)
0170 IF N(11,1)<>8 THEN STOP !data error
0180 DIM A(75),F(72),S(40),S1(40),X(73),X1(73),Z(18),L$(66),L1$(66),M$(70),A$(13)
0190 OPEN FILE (1,2),"Mixtitles",66
0200 GPOS FILE (1),P
0210 LET P=P/66
0220 CLOSE
0230 FOR J0=1 TO P
0240   !
0250   !BUILD-UP
0260   !
0270   LET P9=SYS(5)
0280   LET P8=SYS(0)
0290   OPEN FILE (1,3),"Mixtitles",66
0300   LREAD FILE (1,J0-1),L1$
0310   ON J0 THEN GOTO 3250, 3280
0320   LET I0=POS(L1$,":",3)+1
0330   LET F0=VAL(L1$(POS(L1$,"(",3)+1,I0))
0340   LET F1=VAL(L1$(I0,POS(L1$," ",I0)))
0350   LET F=F0+F1
0360   OPEN FILE (0,3),"Species"
0370   MAT READ FILE (0),X,A
0380   FOR J=1 TO 72
0390     LET X(J)=(X(J)*F0+A(J)*F1)/F
0400   NEXT J
0410   GOSUB 4690
0420   GOSUB 4890
0430   FOR J=1 TO 18
0440     LET Z(J)=(D0(J)*F0+D1(J)*F1)/F
0450   NEXT J
0460   MAT S0=ZER(40)
0470   MAT Z1=ZER(18)
0480   CLOSE
0490   LET D0=0
0500   LET F0=0 ! 1 flag this min finished with
0510   LET F1=0 ! 0 flag 1st time thru each min
0520   LET F3=0 ! 1 flag co-precipitation occurs
0530   PRINT "<12><13>";L1$;"<13><13>"
0540   FOR I0=0 TO 2
0550     LET F2=1 ! 0 flag all done this sample
```

```
ITERATEcont
0560      IF F3=0 THEN IF F1 THEN IF I0=0 THEN GOTO 2280
0570      IF F3=2 THEN LET F3=0
0580      !
0590      !SPECIATE
0600      !
0610      LET M$="PRE-DEPOSITION"
0620      IF I0 THEN LET M$="MINERAL CODE ",STR$(M(F0))
0630      IF F3 THEN LET M$="MINERAL CODES ",STR$(M(F0)),' & ',STR$(M(I1)),' CO-PRECIPITATION"
0640      IF I0=1 THEN LET M$=M$,' : OVER-DEPOSITION"
0650      IF I0=2 THEN LET M$=M$,' : POST-DEPOSITION"
0660      IF J0<3 THEN LET M$="SPECIATION ONLY"
0670      PRINT "<23>";M$;
0680      MAT A=ZER
0690      MAT X=ZER
0700      FOR J=1 TO 72
0710        LET F(J)=1
0720      NEXT J
0730      LET A1=999
0740      FOR J=1 TO 18
0750        LET X(J)=Z(J)
0760      NEXT J
0770      LET A(71)=10↑(-H)
0780      LET X(71)=A(71)
0790      LET X(72)=K(73)/A(71)
0800      LET X(73)=1
0810      REM 1ST EST.OF HCO3
0820      LET X(6)=(Z(6)+X(71)-X(72))/(1+Z(1)*K(21)+Z(2)*K(25)+Z(3)*K(29)+2*(1+Z(1)*K(20)+Z(2)*K(24)+Z(3)*K(28))/(K(6)*A(71)))
0830      IF X(6)<0 THEN PRINT "ALKALINITY IS COMPUTED TO BE ";X(6);" MOLES - POSSIBLE PH OR ALK. ERROR"
0840      IF X(6)<0 THEN STOP
0850      LET M=0
0860      IF M>49 THEN PRINT "NOT CONVERGED AFTER 50 ITERATIONS"
0870      IF M>49 THEN STOP
0880      PRINT  TAB(65);"Iteration";M
0890      PRINT  TAB(60);"<23>";
0900      LET L=Z(6)*10↑-6
0910      REM CALC. I.S. &F(I)
0920      GOSUB 4690
0930      REM CALC.A FOR H2O OH CO3
0940      LET A(72)=K(73)*A(73)/A(71)
0950      LET X(72)=A(72)/F(72)
0960      LET A(34)=A(6)/(K(6)*A(71))
0970      REM TEST FOR CONVERG.
0980      LET A2=A1
0990      LET A1=X(6)+X(20)+X(21)+X(24)+X(25)+X(28)+X(29)+X(34)+X(68)
1000      IF ABS(A1-A2)<L THEN GOTO 1860
1010      LET M=M+1
1020      REM REDOX
1030      LET A(66)=F(66)*0
1040      LET E1=-FNL(K(66))-.5*FNL(A(73))-H+.25*FNL(A(66))
1050      IF A(7)>0 THEN LET C=FNL(K(74))+FNL(A(7))-10*H-8*E1-4*FNL(A(73))
```

ITERATEcont

```
1060     IF A(7)>0 THEN IF C>-75 THEN LET A(17)=10↑C
1070     IF A(17)>0 THEN LET A(17)=Z(17)/(1/F(17)+K(62)*(1/F(62)+K(63)/(F(63)*A(71)))/A(71))
1080     LET A(62)=K(62)*A(17)/A(71)
1090     LET A(63)=K(63)*A(62)/A(71)
1100     REM SIO2 SPEC.
1110     LET A(14)=Z(14)/(1/F(14)+(K(37)/F(37)+K(38)/F(38))/A(71))
1120     LET A(37)=K(37)*A(14)/A(71)
1130     LET A(38)=K(38)*A(14)/(A(71)*A(71))
1140     REM B SPEC.
1150     LET A(15)=Z(15)/(1/F(15)+K(44)/(F(44)*A(71)))
1160     LET A(44)=K(44)*A(15)/A(71)
1170     REM AL SPEC.
1180     LET C=A(72)*A(72)*(A(72)*A(72)*K(8)/F(8)+K(40)/(F(40)*A(72))+K(41)/F(41))
1190     LET A(39)=Z(8)/(1/F(39)+C+A(7)*(K(42)/F(42)+K(43)*A(7)/F(43)))
1200     LET C=A(39)*A(72)
1210     LET A(8)=K(8)*C*A(72)↑3
1220     LET A(40)=K(40)*C
1230     LET A(41)=K(41)*C*A(72)
1240     LET A(42)=K(42)*A(39)*A(7)
1250     LET A(43)=K(43)*A(39)*A(7)*A(7)
1260     REM FE SPEC.
1270     LET E=10↑(-E1)
1280     LET A(74)=E
1290     LET C=A(71)/A(73)
1300     LET G=C*C
1310     LET Y=E/F(52)+K(9)/(F(9)*C*G)
1320     LET Y=Y+K(45)/F(45)+K(46)*A(5)/F(46)+K(47)*A(5)↑3/F(47)+K(48)/(F(48)*C)+K(49)/(F(49)*G)
1330     LET Y=Y+K(50)/(F(50)*G*G)+K(51)*A(7)/F(51)+K(53)*A(5)*A(5)/F(53)+K(54)*E/(F(54)*C)
1340     LET Y=Y+K(55)*E/(F(55)*G)+K(56)*E/(F(56)*G*A(71))
1350     LET A(52)=E*Z(9)/(Y+K(57)*E*A(7)/F(57))
1360     IF E=0 THEN GOTO 1470
1370     LET Y=A(52)/E
1380     LET A(9)=K(9)*Y/(C*G)
1390     LET A(45)=K(45)*Y
1400     LET A(46)=K(46)*Y*A(5)
1410     LET A(47)=K(47)*Y*(A(5)↑3)
1420     LET A(48)=K(48)*Y/C
1430     LET A(49)=K(49)*Y/G
1440     LET A(50)=K(50)*Y/(G*G)
1450     LET A(51)=K(51)*Y*A(7)
1460     LET A(53)=K(53)*Y*A(5)*A(5)
1470     LET A(54)=K(54)*A(52)/C
1480     LET A(55)=K(55)*A(52)/G
1490     LET A(56)=K(56)*A(52)/(G*A(71))
1500     LET A(57)=K(57)*A(52)/A(7)
1510     REM N SPEC. REDOX EQUI. NOT ASSUMED
1520     IF Z(18)>0 THEN LET A(18)=Z(18)/(1/F(18)+K(64)/(F(64)*A(71))+K(65)/(F(65)*A(7)))
1530     IF A(18)>0 THEN LET A(64)=K(64)*A(18)/A(71)
1540     IF A(18)>0 THEN LET A(65)=K(65)*A(18)/A(7)
1550     REM ALL OTHER ION-PAIRS
```

```
ITERATEcont
1560      FOR J=1 TO 21
1570        LET A(P(J))=K(P(J))*A(I1(J))*A(I2(J))
1580      NEXT J
1590      LET A(36)=K(36)*A(71)*A(71)*A(7)
1600      FOR J=8 TO 72
1610        LET X(J)=A(J)/F(J)
1620      NEXT J
1630      REM KEY SPEC.
1640      LET Y=19
1650      FOR J=1 TO 3
1660        IF X(J)>0 THEN LET C=X(J)
1670        IF X(J)>0 THEN LET X(J)=Z(J)/(1+(X(Y)+X(Y+1)+X(Y+2)+X(Y+3))/C)
1680        LET Y=Y+4
1690      NEXT J
1700      IF X(4)>0 THEN LET C=X(4)
1710      IF X(4)>0 THEN LET X(4)=Z(4)/(1+(X(31)+X(32))/C)
1720      IF X(5)>0 THEN LET C=X(5)
1730      IF X(5)>0 THEN LET X(5)=Z(5)/(1+(X(27)+X(31)+X(33)+X(46)+3*X(47)+2*X(53))/C)
1740      IF X(7)>0 THEN LET C=X(7)
1750      IF X(7)>0 THEN LET X(7)=Z(7)/(1+(X(22)+X(26)+X(30)+X(32)+X(35)+X(36)+X(42)+2*X(43)+X(51)+X(57)+X(61)+X(65))/C)
1760      IF X(10)>0 THEN LET C=X(10)
1770      IF X(10)>0 THEN LET X(10)=Z(10)/(1+X(58)/C)
1780      IF X(11)>0 THEN LET C=X(11)
1790      IF X(11)>0 THEN LET X(11)=Z(11)/(1+X(59)/C)
1800      IF X(12)>0 THEN LET C=X(12)
1810      IF X(12)>0 THEN LET X(12)=Z(12)/(1+(X(60)+X(61))/C)
1820      LET Y=X(37)+2*X(38)+X(44)+X(40)+2*X(41)+4*X(8)+X(62)+2*X(63)+X(64)+X(72)+X(19)+X(23)+X(58)+X(59)+X(60)
1830      LET C=X(6)
1840      LET X(6)=(Z(6)+X(71)+X(33)+X(35)+2*X(36)-Y)/(1+(X(21)+X(25)+X(29)+2*(X(20)+X(24)+X(28)+X(34)))/C)
1850      GOTO 0860
1860      LET A(75)=1
1870      LET P1=99.99
1880      LET C=0
1890      LET G=0
1900      FOR J=1 TO 72
1910        IF C(J)>0 THEN LET C=C+C(J)*X(J)
1920        IF C(J)<0 THEN LET G=G-C(J)*X(J)
1930      NEXT J
1940      LET P2=FNL(K(77))-FNL(A(68))
1950      LET E1=100*(C-G)/(C+G)
1960      PRINT "<13>Iteration complete"
1970      IF F1 THEN GOTO 2080
1980      IF D0 THEN GOTO 2070
1990      IF J0>2 THEN GOTO 2030
2000      OPEN FILE (0,J0),"Species"
2010      MAT WRITE FILE (0),X
2020      GOTO 2060
2030      OPEN FILE (0,1),"Analysis"
2040      MAT WRITE FILE (0),Z,X,F
2050      WRITE FILE (0),T,0,H,U,E1
```

ITERATEcont

```
2060     CLOSE
2070     LET F1=1
2080     FOR J=1 TO 40
2090       LET S(J)=-99.99
2100       IF N1(J)=0 THEN GOTO 2210
2110       IF A(S1(J))=0 THEN GOTO 2210
2120       IF N2(J) THEN IF A(S2(J))=0 THEN GOTO 2210
2130       IF N3(J) THEN IF A(S3(J))=0 THEN GOTO 2210
2140       IF N4(J) THEN IF A(S4(J))=0 THEN GOTO 2210
2150       LET S(J)=N1(J)*FNL(A(S1(J)))+K3(J)
2160       IF N2(J) THEN LET S(J)=S(J)+N2(J)*FNL(A(S2(J)))
2170       IF N3(J) THEN LET S(J)=S(J)+N3(J)*FNL(A(S3(J)))
2180       IF N4(J) THEN LET S(J)=S(J)+N4(J)*FNL(A(S4(J)))
2190       IF J=26 THEN IF S(26)>-99.99 THEN LET S(26)=S(26)+3*FNL(A(2))
2200       IF J=39 THEN IF S(39)>-99.99 THEN LET S(39)=S(39)+.25*FNL(A(2))
2210     NEXT J
2220     !
2230     !**IDENTI-MIN**
2240     !
2250     IF J0<3 THEN LET F2=0
2260     IF J0<3 THEN GOTO 2420
2270     IF F0 THEN GOTO 2420
2280     LET I=1
2290     LET C=0
2300     LET X=0
2310     LET L=-1
2320     FOR J=1 TO 12
2325       IF J=11 THEN GOTO 2380
2330       LET G=M(J)
2340       IF S(G)>.04 THEN LET L=K3(G)/(N1(G)+N2(G)+N3(G))
2350       IF S0(G) THEN IF S(G)<-.04 THEN LET X=J
2360       IF L>C THEN LET I=J
2370       IF L>C THEN LET C=L
2380     NEXT J
2390     IF X THEN GOTO 5630
2400     IF S(M(I))<=.04 THEN LET F2=0 ! within 10% of full deposition
2410     LET F0=I
2420     !
2430     !
2440     !**PRINT OUT**
2450     !
2460     ON ERR THEN GOTO 3310
2470     OPEN FILE (0,3),"$LPT"
2480     ON ERR THEN STOP
2490     OPEN FILE (1,3),"Specminz"
2500     IF F2=0 THEN PRINT FILE (0),"<27><";L1$;"<13><13>SPECIATION <27>=<13>"
2510     IF F2=0 THEN GOTO 2540
2520     PRINT FILE (0),"<27><";L1$;"<13>SPECIES FOUND AFTER";M;" ITERATIONS"
2530     PRINT FILE (0),"FOR ";M$;"<27>="
2540     PRINT FILE (0),"SPECIES     CONCENTRATION        SPECIES     CONCENTRATION        SPECIES     CONCENTRATION"
```

ITERATEcont

```
2550      LET W=0
2560      FOR J=1 TO 72
2570        LREAD FILE (1),L$
2580        IF X(J)=0 THEN GOTO 2630
2590        LET W=W+1
2600        PRINT FILE (0), TAB(W*33-32);L$; TAB(W*33-20);X(J);
2610        IF W/3=INT(W/3) THEN PRINT FILE (0),
2620        IF W/3=INT(W/3) THEN LET W=0
2630      NEXT J
2640      PRINT FILE (0),"<13>Temp.(C)     ";T
2650      LET L$=""
2660      IF F2 THEN PRINT FILE (0),"<13><27><KEY MINERAL STATUS<27>="
2670      IF F2=0 THEN PRINT FILE (0),"<13><27><MINERALS FORMED<27>="
2680      PRINT FILE (0),"MINERAL"; TAB(18);"SAT.INDEX     MOLES"; TAB(48);"MINERAL"; TAB(66);"SAT.INDEX     MOLES"
2690      LET G=1
2700      LET W=0
2710      FOR J=1 TO 40
2720        LREAD FILE (1),L$
2730        IF L$="" THEN GOTO 2830
2740        LET A$=STR$(S0(J))
2750        IF F2=0 THEN GOTO 5880
2760        IF J<>M(G) THEN GOTO 2830
2770        PRINT FILE (0), TAB(W*48);L$;
2780        PRINT FILE (0), TAB(W*48+17);S(J); TAB(W*48+31);A$;
2790        LET W=W+1
2800        IF W=2 THEN PRINT FILE (0),
2810        IF W=2 THEN LET W=0
2820        IF G<12 THEN LET G=G+1
2830      NEXT J
2840      PRINT FILE (0),"<13><13><27><TOTAL DETERMINAND CONCENTRATIONS<27>="
2850      IF F2 THEN GOTO 5700
2860      IF J0<3 THEN GOTO 5700
2870      PRINT FILE (0),"DETERMINAND"; TAB(22);"ORIGINAL     FINAL          DETERMINAND"; TAB(70);"ORIGINAL     FINAL"
2880      OPEN FILE (2,3),"Analysis"
2890      MAT READ FILE (2),Z1,X,F
2900      READ FILE (2),T,0,A,B,C
2910      LET W=0
2920      FOR J=1 TO 18
2930        LREAD FILE (1),L$
2940        IF L$="" THEN GOTO 2990
2950        PRINT FILE (0), TAB(W*48);L$; TAB(W*48+21);Z1(J); TAB(W*48+34);Z(J);
2960        LET W=W+1
2970        IF W=2 THEN PRINT FILE (0),
2980        IF W=2 THEN LET W=0
2990      NEXT J
3000      PRINT FILE (0), TAB(1);"pH"; TAB(21);A; TAB(34);H
3010      PRINT FILE (0),"ionic strength"; TAB(21);B; TAB(34);U
3020      PRINT FILE (0),"charge error (%)"; TAB(21);C; TAB(34);E1
3030      PRINT FILE (0),"<13><27><All concentrations expressed in moles <27>="
3040      PRINT FILE (0),USING "date          : ff/ff/ff     time     : ff:ff:ff",SYS(1),SYS(2),SYS(3)-1900,SYS(11),SYS(12),SYS(13)
```

```
ITERATEcont
3050      PRINT FILE (0),USING "elapsed secs: ffff        cpu used: ffff.f",SYS(0)-P8,SYS(5)-P9
3060      CLOSE
3070      IF F2=0 THEN LET I0=2
3080      IF F2=0 THEN GOTO 3200
3090      LET I=F0
3100      GOSUB 4530
3110      ON I0 THEN GOTO 3370, 3560
3120      !
3130      !**OVER-DEPOSITION**
3140      !
3150      LET D0=X
3160      LET N0=L
3170      LET S5=S(M(I))
3180      LET Z5=Z(N(I,1))
3190      GOSUB 5400
3200    NEXT I0
3210    IF F2 THEN GOTO 0540
3220 NEXT J0
3230 CLOSE
3240 STOP !fini
3250 MAT Z=D0
3260 LET H=H0
3270 GOTO 0460
3280 MAT Z=D1
3290 LET H=H1
3300 GOTO 0460
3310 DELAY =10
3320 PRINT "WAITING FOR LINEPRINTER"
3330 RETRY
3335 STOP
3340 !
3350 !**POST-DEPOSITION**
3360 !
3370 LET Z6=Z(N(I,1))
3380 LET S6=S(M(I))
3390 LET Z1(I)=(FNL(Z5)-FNL(Z6))/(S5-S6) !slope for M(I)
3400 LET G=Z6*(10↑((.01-S6)*Z1(I))-1)/N(I,2) !to within 5%
3410 LET G=-G
3420 GOSUB 4660
3430 GOSUB 5190
3440 GOSUB 5100
3450 IF X<>34 THEN IF Y<>72 THEN GOTO 3470
3460 GOSUB 4900
3470 LET D0=F0
3480 LET S0(M(D0))=S0(M(D0))+(Z5-Z(N(D0,1)))/N(D0,2)
3500 GOTO 3200
3530 !
3540 !**IDENTI-CO-MIN**
3550 !
3560 LET X=0
```

ITERATEcont
```
3570 IF F3 THEN GOSUB 3790
3580 IF F3 THEN GOTO 3630
3590 IF S(M(D0))<-.04 THEN GOTO 5610
3600 FOR I=1 TO 12
3610   IF I<>F0 THEN IF S0(M(I)) THEN IF S(M(I))<-.04 THEN GOSUB 3650
3620 NEXT I
3630 IF X=0 THEN LET F0=0
3640 GOTO 3200
3650 LET I1=I
3660 LET D1=0
3670 LET D2=0
3680 LET C=M(I)
3690 LET G=M(F0)
3700 IF S1(C)<>34 THEN LET D1=S1(C)
3710 IF D1=0 THEN IF S2(C)<>72 THEN LET D1=S2(C)
3720 IF D1=0 THEN LET D1=S3(C)
3730 IF S1(G)<>34 THEN IF D1<>S1(G) THEN LET D2=S1(G)
3740 IF D2=0 THEN IF S2(G)<>72 THEN IF D1<>S2(G) THEN LET D2=S2(G)
3750 IF D2=0 THEN IF D1<>S3(G) THEN LET D2=S3(G)
3760 IF D2=0 THEN LET D2=6
3770 IF D1=39 THEN LET D1=8
3780 IF D2=39 THEN LET D2=8
3790 LET Z1(F3+13)=Z(D1)
3800 LET Z1(F3+15)=Z(D2)
3810 LET Z1(F3+17)=S(M(I1))
3820 IF F3 THEN GOTO 4040
3830 GOSUB 4530
3840 LET G=.1*S0(M(I))
3850 LET S0(M(I))=S0(M(I))-G
3860 LET G=-G
3870 GOSUB 4660
3880 GOSUB 5190
3890 GOSUB 5100
3900 IF X<>34 THEN IF Y<>72 THEN GOTO 3920
3910 GOSUB 4900
3920 IF F2=0 THEN LET I1=0
3930 IF F2=0 THEN GOTO 0550
3940 LET F0=D0
3950 LET X=1
3960 LET F3=F3+1
3970 LET I=12
3980 IF F3<2 THEN RETURN
3990 LET F0=0
4000 RETURN
4010 !
4020 !**CO-PRECIPITATE**
4030 !
4040 LET A=Z1(18)-Z1(17)
4050 LET C=Z1(14)*(10↑(-Z1(18)*(FNL(Z1(14))-FNL(Z1(13)))/A)-1)
4060 LET Z(D1)=Z(D1)+C
```

ITERATEcont

```
4070 LET G=Z1(16)*(10↑(-Z1(18)*(FNL(Z1(16))-FNL(Z1(15)))/A)-1)
4080 LET Z(D2)=Z(D2)+G
4090 FOR J=0 TO 1
4100   LET W=M(I1)
4110   IF J THEN LET W=M(D0)
4120   FOR U=0 TO 1
4130     LET B=D1
4140     IF U THEN LET B=D2
4150     IF B=6 THEN LET B=34
4160     IF B=8 THEN LET B=39
4170     LET Z=0
4180     IF B=S1(W) THEN LET Z=N1(W)
4190     IF B=S2(W) THEN LET Z=N2(W)
4200     IF B=S3(W) THEN LET Z=N3(W)
4210     LET Z1(U+13)=B !spec no for D1,D2
4220     LET Z1(U+2*J+15)=Z !stoich no for D1inI1,D2inI1,D1inD0,D2inD0
4230   NEXT U
4240 NEXT J
4250 LET X(Z1(13))=X(Z1(13))+C
4260 LET X(Z1(14))=X(Z1(14))+G
4270 LET A=(G*Z1(17)-C*Z1(18))/(Z1(16)*Z1(17)-Z1(15)*Z1(18))
4280 LET B=(C-A*Z1(15))/Z1(17)
4290 LET S0(M(D0))=S0(M(D0))-B !deposited
4300 LET S0(M(I1))=S0(M(I1))-A !redissolved
4310 LET C=Z1(13)
4320 LET G=Z1(14)
4330 FOR J=0 TO 1
4340   LET I=I1
4350   IF J THEN LET I=D0
4360   LET W=A
4370   IF J THEN LET W=B
4380   GOSUB 4530
4390   IF X<>C THEN IF X<>G THEN LET X(X)=X(X)+L*W
4400   IF Y<>C THEN IF Y<>G THEN LET X(Y)=X(Y)+M*W
4410   IF N THEN IF Z<>C THEN IF Z<>G THEN LET X(Z)=X(Z)+N*W
4420   IF X=34 THEN LET X=6
4430   IF X=39 THEN LET X=8
4440   IF Y=72 THEN LET Y=6
4450   IF X<>D1 THEN IF X<>D2 THEN LET Z(X)=Z(X)+L*W
4460   IF Y<>D1 THEN IF Y<>D2 THEN LET Z(Y)=Z(Y)+M*W
4470   IF N THEN IF Z<>D1 THEN IF Z<>D2 THEN LET Z(Z)=Z(Z)+N*W
4480 NEXT J
4490 GOSUB 4690
4500 GOSUB 5190
4510 LET Z(6)=A
4520 GOTO 3950
4530 !
4540 !**SUB AFFECTED SPECIES**
4550 !
4560 LET X=S1(M(I))
```

ITERATE cont
```
4570 LET Y=S2(M(I))
4580 LET Z=S3(M(I))
4590 LET L=N1(M(I))
4600 LET M=N2(M(I))
4610 LET N=N3(M(I))
4620 RETURN
4630 !
4640 !SUB ADJUST SPECIES & ION STRENGTH
4650 !
4660 LET X(X)=X(X)-G*L
4670 LET X(Y)=X(Y)-G*M
4680 IF N THEN LET X(Z)=X(Z)-G*N
4690 LET U=0
4700 FOR J=1 TO 72
4710   LET U=U+.5*X(J)*C(J)*C(J)
4720 NEXT J
4730 LET C=0
4740 FOR J=1 TO 72
4750   LET W=0
4760   IF J<8 THEN LET W=B(J)
4770   IF C(J)=0 THEN LET F(J)=10↑(.1*U)
4780   IF C(J) THEN LET F(J)=10↑(-SQR(U)*C(J)*C(J)*A9/(1+B9*SQR(U)*R(J))+U*W)
4790   IF J<>71 THEN LET A(J)=F(J)*X(J)
4800   LET C=C+X(J)
4810 NEXT J
4820 LET A(73)=1-.017*C
4830 LET C=T*T
4840 LET F(68)=10↑(U*(33.5-.109*T+.0014*C-U*(1.5+.015*T-.0004*C))/(T+273.15))
4850 RETURN
4860 !
4870 !**SUB pH**
4880 !
4890 GOSUB 5190
4900 LET W=C
4910 LET C=B+Q+X(6)+X(34)+X(68)
4920 LET K=K(68)*F(6)*F(6)/(K(6)*F(34)*F(68))
4930 LET L=X(34)*.000001
4940 LET M=1+B/X(34)
4950 LET N=1+Q/X(6)
4960 LET Y=A-W-X(72)+X(71)
4970 LET X=SQR((K*Y*Y-((C-Y)*N*N+4*K*M*Y)*X(34))/(M*(N*N-4*K*M)))
4980 LET X(6)=(Y-2*M*X)/N
4990 LET X(71)=X(6)*F(6)/(K(6)*X*F(34)*F(71))
5000 LET X(72)=K(73)*A(73)/(X(71)*F(71)*F(72))
5010 IF ABS(X-X(34))<L THEN GOTO 5040
5020 LET X(34)=X
5030 GOTO 4930
5040 LET X(68)=K*X(6)*X(6)/X(34)
5050 LET H=-FNL(X(71)*F(71))
5060 RETURN
```

ITERATE:cont
```
5070 !
5080 !**SUB ADJUST TOTALS**
5090 !
5100 IF X=39 THEN LET X=8
5110 IF X<>34 THEN LET Z(X)=Z(X)-G*L
5120 IF Y<>72 THEN LET Z(Y)=Z(Y)-G*M
5130 IF N THEN LET Z(Z)=Z(Z)-G*N
5140 LET Z(6)=A
5150 RETURN
5160 !
5170 !**SUB ALKALINITY**
5180 !
5190 LET B=X(20)+X(24)+X(28)
5200 LET Q=X(21)+X(25)+X(29)
5210 LET C=X(37)+X(40)+X(19)+X(23)+2*(X(38)+X(41)+2*X(8))
5220 LET A=Q+C+X(6)+X(72)-X(71)+2*(B+X(34))
5230 RETURN
5240 LET I=X
5250 LET I1=X
5260 GOTO 3830
5270 MAT Z=D0
5280 LET H=H0
5290 GOTO 0460
5300 MAT Z=D1
5310 LET H=H1
5320 GOTO 0460
5330 DELAY =10
5340 PRINT "WAITING FOR LINEPRINTER"
5350 RETRY
5360 STOP
5370 !
5380 !***SUB ADJUST DEPOSITION***
5390 !
5400 LET W=0
5410 IF X<19 THEN LET C=Z(X)
5420 IF X=39 THEN LET C=Z(8)
5430 IF X=34 THEN LET C=X(34)
5440 IF Y<19 THEN LET D=Z(Y)
5450 IF Y<>72 THEN IF D*M<C*L THEN LET D0=Y
5460 IF D0=Y THEN LET N0=M
5470 IF D0=Y THEN LET C=D
5480 IF N THEN IF Z(Z)*N<C*N0 THEN LET D0=Z
5490 IF D0=Z THEN LET N0=N
5500 IF D0=39 THEN LET G=Z(8)
5510 IF D0=34 THEN LET G=X(34)
5520 IF D0<>34 THEN IF D0<>39 THEN LET G=Z(D0)
5530 LET G=G/N0*(1-10↑-S5)
5540 IF W THEN LET G=-G
5550 GOSUB 4660
5560 GOSUB 5190
```

ITERATEcont

```
5570 GOSUB 5100
5580 IF X<>34 THEN IF Y<>72 THEN RETURN
5590 GOSUB 4900
5600 RETURN
5610 LET X=D0
5620 LET I0=0
5630 LET I=X
5640 LET S5=-S(M(I))
5650 GOSUB 4530
5660 LET W=1
5670 GOSUB 5410
5680 LET S0(M(I))=S0(M(I))+G/N0
5690 GOTO 0610
5700 !
5710 !**SUB PRINT OUT**
5720 !
5730 TAB =23
5740 PRINT FILE (0),"DETERMINAND"," ANALYSIS","DETERMINAND"," ANALYSIS"
5750 LET W=0
5760 FOR J=1 TO 18
5770   LREAD FILE (1),L$
5780   IF L$="" THEN GOTO 5820
5790   PRINT FILE (0),L$,Z(J),
5800   LET W=W+1
5810   IF W/2=INT(W/2) THEN PRINT FILE (0)
5820 NEXT J
5830 PRINT FILE (0)
5840 PRINT FILE (0),"<13>pH                ",H
5850 PRINT FILE (0),"ionic strength",U,"charge error",E1;"%"
5860 TAB =14
5870 GOTO 3030
5880 IF A$="0" THEN IF S(J)>-.04 THEN LET A$="not assessed"
5890 IF A$="0" THEN GOTO 2830
5900 GOTO 2770
```

dated: 14 / 10 / 1985

APPENDIX F

OPERATION OF SPECIATION MODEL

TABLE F.1. Printouts generated by WATDEPOSIT including a forced printout of speciation prior to mineral deposition.

North Inlet

SPECIATION

SPECIES	CONCENTRATION	SPECIES	CONCENTRATION	SPECIES	CONCENTRATION
Ca++	1.00482E-03	Mg++	8.57144E-04	Na+	9.01628E-04
K+	1.70932E-05	Cl-	7.33351E-04	HCO3-	2.62256E-03
SO4--	6.17885E-04	Al(OH)4-	6.29776E-06	Fe(OH)3	8.55365E-07
NO3-	5.18915E-04	H4SiO4	1.63458E-04	H3BO3	5.5499E-06
NH4+	3.67366E-10	CaOH+	8.05147E-09	CaCO3	8.34996E-06
CaHCO3+	1.32674E-05	CaSO4	5.63903E-05	MgOH+	4.21881E-08
MgCO3	4.97022E-06	MgHCO3+	1.74211E-05	MgSO4	4.17776E-05
NaCl	1.38247E-08	NaCO3-	8.7585E-08	NaHCO3	1.11627E-06
NaSO4-	1.89538E-06	KCl	2.71965E-10	KSO4-	4.1253E-08
HCl	1.00727E-18	CO3--	1.46846E-05	HSO4-	2.58554E-10
H2SO4	1.27437E-21	H3SiO4-	1.30822E-06	H2SiO4--	8.27722E-11
Al+++	1.56884E-14	AlOH++	4.20721E-12	Al(OH)2+	2.96364E-09
AlSO4+	4.88883E-15	Al(SO4)2-	1.59708E-16	H2BO3-	4.46985E-14
Fe+++	1.49653E-17	FeCl++	9.42682E-20	FeCl3	5.72049E-26
FeOH++	2.0387E-12	Fe(OH)2+	1.85434E-08	Fe(OH)4-	5.58574E-07
FeSO4+	2.91024E-17	Fe++	5.17691E-18	FeCl2+	9.44949E-22
FeOH+	8.79344E-20	Fe(OH)2	1.74566E-23	FeOOH-	2.20959E-24
FeSO4	1.28122E-12	NH3	9.1462E-12	NH4SO4-	1.07063E-05
O2	3.125E-04	H2CO3	5.31717E-05	H+	8.59459E-09
OH-	4.95566E-07				
Temp.(C)	12				

MINERALS FORMED

MINERAL	SAT.INDEX	MOLES	MINERAL	SAT.INDEX	MOLES
calcite	.283243	not assessed	aragonite	-1.30777E-02	not assessed
gibbsite	.109131	not assessed	quartz	.426977	not assessed
dolomite	.417644	not assessed	goethite	5.88902	not assessed
boehmite	.663422	not assessed	adularia	.197236	not assessed
muscovite	3.27705	not assessed	talc	.946507	not assessed
kaolinite	4.30274	not assessed	halloysite	6.33945E-02	not assessed
chlorite	10.4129	not assessed	pyrophyllite	.608845	not assessed
illite	3.43003	not assessed	montmorillonite	4.11471	not assessed

TOTAL DETERMINAND CONCENTRATIONS

DETERMINAND	ANALYSIS	DETERMINAND	ANALYSIS
calcium	1.08283E-03	magnesium	9.21356E-04
sodium	9.04741E-04	potassium	1.71347E-05
chloride	7.33365E-04	alkalinity(asHCO3)	2.73759E-03
sulphate	7.28696E-04	aluminium	6.30073E-06
iron	1.43248E-06	nitrate	5.18915E-04
silica	1.64767E-04	boron	5.5499E-06
ammonia	1.07066E-05		

pH	8.1		
ionic strength	7.41193E-03	charge error	-4.96148 %

All concentrations expressed in moles

date : 14/10/85 time : 12:23:31

elapsed secs: 43 cpu used: 37.6

Leachate

SPECIATION

SPECIES	CONCENTRATION	SPECIES	CONCENTRATION	SPECIES	CONCENTRATION
Ca++	2.03154E-05	Mg++	9.7946E-06	Na+	8.01402E-02
K+	6.49252E-04	Cl-	1.91013E-03	HCO3-	2.62093E-04
SO4--	4.14633E-03	Al(OH)4-	5.18884E-03	Fe(OH)3	2.83752E-10
NO3-	1.56317E-04	H4SiO4	2.63487E-06	H3BO3	7.58407E-05
NH4+	6.49367E-09	CaOH+	1.01666E-06	CaCO3	7.69991E-05
CaHCO3+	1.47668E-08	CaSO4	2.20289E-06	MgOH+	3.1024E-06
MgCO3	2.68556E-05	MgHCO3+	1.17011E-08	MgSO4	9.5629E-07
NaCl	2.24307E-06	NaCO3-	6.50892E-03	NaHCO3	7.14001E-06
NaSO4-	5.96709E-04	KCl	1.844E-08	KSO4-	5.42727E-06
HCl	2.19779E-22	CO3--	2.25351E-02	HSO4-	1.10929E-13
H2SO4	4.6437E-29	H3SiO4-	2.5034E-04	H2SiO4--	2.38042E-04
Al+++	3.30871E-27	AlOH++	5.79488E-21	Al(OH)2+	2.53348E-14
AlSO4+	1.58472E-27	Al(SO4)2-	1.84235E-28	H2BO3-	8.01507E-09
Fe+++	1.49313E-32	FeCl++	1.40503E-34	FeCl3	2.12125E-40
FeOH++	1.35899E-23	Fe(OH)2+	7.49922E-16	Fe(OH)4-	2.14844E-06
FeSO4+	4.42899E-32	Fe++	3.25316E-29	FeCl2+	1.9214E-36
FeOH+	3.56022E-27	Fe(OH)2	5.7646E-27	FeOOH-	8.5259E-24
FeSO4	1.25002E-24	NH3	1.17663E-06	NH4SO4-	4.73536E-05
O2	3.125E-04	H2CO3	4.56038E-10	H+	9.83213E-13
OH-	5.79233E-03				
Temp.(C)	12				

MINERALS FORMED

MINERAL	SAT.INDEX	MOLES	MINERAL	SAT.INDEX	MOLES
calcite	1.25777	not assessed	aragonite	.961447	not assessed
magnesite	.580108	not assessed	brucite	1.33274	not assessed
dolomite	2.13455	not assessed	huntite	.133301	not assessed
goethite	2.41953	not assessed	phlogopite	10.8088	not assessed
muscovite	-1.52702E-02	not assessed	talc	11.2037	not assessed
chlorite	24.8902	not assessed	hydromagnesite	4.50035	not assessed

TOTAL DETERMINAND CONCENTRATIONS

DETERMINAND	ANALYSIS	DETERMINAND	ANALYSIS
calcium	1.00549E-04	magnesium	4.07206E-05
sodium	8.72553E-02	potassium	6.54698E-04
chloride	1.91239E-03	alkalinity(asHCO3)	8.58445E-02
sulphate	4.79898E-03	aluminium	5.18884E-03
iron	2.14873E-06	nitrate	1.56317E-04
silica	2.52975E-04	boron	7.58487E-05
ammonia	4.85367E-05		

pH	12.09		
ionic strength	.104656	charge error	4.05 %

All concentrations expressed in moles

date : 14/10/85 time : 12:22:48

elapsed secs: 87 cpu used: 66.4

Loch Body (1:7.71 Leachate:North Inlet)
SPECIES FOUND AFTER 13 ITERATIONS
FOR PRE-DEPOSITION

SPECIES	CONCENTRATION	SPECIES	CONCENTRATION	SPECIES	CONCENTRATION
Ca++	4.23074E-04	Mg++	4.23665E-04	Na+	1.06031E-02
K+	9.00035E-05	Cl-	8.6855E-04	HCO3-	1.7933E-03
SO4--	1.08845E-03	Al(OH)4-	6.0131E-04	Fe(OH)3	8.69309E-09
NO3-	4.77285E-04	H4SiO4	5.58681E-05	H3BO3	1.36209E-05
NH4+	7.95071E-10	CaOH+	7.76136E-07	CaCO3	5.11749E-04
CaHCO3+	3.30378E-06	CaSO4	3.11537E-05	MgOH+	4.79373E-06
MgCO3	3.59416E-04	MgHCO3+	5.14124E-06	MgSO4	2.72332E-05
NaCl	1.77774E-07	NaCO3-	1.73253E-04	NaHCO3	8.32139E-06
NaSO4-	3.37972E-05	KCl	1.56185E-09	KSO4-	3.28514E-07
HCl	4.4775E-21	CO3--	2.85718E-03	HSO4-	1.5969E-12
H2SO4	2.96028E-26	H3SiO4-	1.19026E-04	H2SiO4--	2.13607E-06
Al+++	4.42176E-22	AlOH++	2.68297E-17	Al(OH)2+	4.33144E-12
AlSO4+	1.66752E-22	Al(SO4)2-	8.27227E-24	H2BO3-	2.95498E-11
Fe+++	1.19345E-26	FeCl++	7.60574E-29	FeCl3	5.14399E-35
FeOH++	3.69133E-19	Fe(OH)2+	7.66834E-13	Fe(OH)4-	1.50602E-06
FeSO4+	2.80549E-26	Fe++	9.29062E-25	FeCl2+	7.7659E-31
FeOH+	3.63791E-24	Fe(OH)2	1.77332E-25	FeOOH-	5.96129E-24
FeSO4	1.31456E-19	NH3	4.79335E-09	NH4SO4-	1.50443E-05
O2	3.125E-04	H2CO3	1.36979E-07	H+	3.46575E-11
OH-	1.31759E-04				
Temp.(C)	12				

KEY MINERAL STATUS

MINERAL	SAT.INDEX	MOLES	MINERAL	SAT.INDEX	MOLES
calcite	2.07158	0	aragonite	1.77526	0
anhydrite	-2.34159	0	magnesite	1.69791	0
brucite	-1.56202E-02	0	gibbsite	-.33458	0
dolomite	4.06616	0	gypsum	-2.15016	0
nesquehonite	-1.27703	0	huntite	4.30051	0
boehmite	.21971	0	hydromagnesite	6.5054	0

TOTAL DETERMINAND CONCENTRATIONS

DETERMINAND	ANALYSIS	DETERMINAND	ANALYSIS
calcium	9.70057E-04	magnesium	8.20249E-04
sodium	1.08187E-02	potassium	9.03337E-05
chloride	8.6873E-04	alkalinity(asHCO3)	1.22791E-02
sulphate	1.19601E-03	aluminium	6.0131E-04
iron	1.51472E-06	nitrate	4.77285E-04
silica	1.74894E-04	boron	1.36209E-05
ammonia	1.50499E-05		
pH	10.5072		
ionic strength	1.70502E-02	charge error	1.18294 %

All concentrations expressed in moles

date : 14/10/85 time : 12:25: 2

elapsed secs: 90 cpu used: 84.7

Loch Body (1:7.71 Leachate:North Inlet)

SPECIATION

SPECIES	CONCENTRATION	SPECIES	CONCENTRATION	SPECIES	CONCENTRATION
Ca++	4.7439E-06	Mg++	5.87244E-06	Na+	.010646
K+	8.99719E-05	Cl-	8.68546E-04	HCO3-	1.8769E-03
SO4--	1.14259E-03	Al(OH)4-	6.0131E-04	Fe(OH)3	1.27644E-08
NO3-	4.77285E-04	H4SiO4	7.15173E-05	H3BO3	1.36209E-05
NH4+	8.66819E-10	CaOH+	6.16494E-09	CaCO3	4.34401E-06
CaHCO3+	4.04075E-08	CaSO4	3.98896E-07	MgOH+	4.70069E-08
MgCO3	3.76524E-06	MgHCO3+	7.74932E-08	MgSO4	4.30338E-07
NaCl	1.82655E-07	NaCO3-	1.2637E-04	NaHCO3	8.93675E-06
NaSO4-	3.71843E-05	KCl	1.59909E-09	KSO4-	3.60165E-07
HCl	6.60124E-21	CO3--	1.99121E-03	HSO4-	2.51944E-12
H2SO4	6.88111E-26	H3SiO4-	1.03376E-04	H2SiO4--	1.23661E-06
Al+++	1.86711E-21	AlOH++	8.03832E-17	Al(OH)2+	9.19056E-12
AlSO4+	8.21222E-22	Al(SO4)2-	4.46214E-23	H2BO3-	1.99698E-11
Fe+++	5.02255E-26	FeCl++	3.34192E-28	FeCl3	2.41464E-34
FeOH++	1.10102E-18	Fe(OH)2+	1.62165E-12	Fe(OH)4-	1.50195E-06
FeSO4+	1.37753E-25	Fe++	2.77917E-24	FeCl2+	3.56294E-30
FeOH+	7.69259E-24	Fe(OH)2	2.60436E-25	FeOOH-	5.94445E-24
FeSO4	3.73762E-19	NH3	3.64648E-09	NH4SO4-	1.50454E-05
O2	3.125E-04	H2CO3	2.11109E-07	H+	5.0058E-11
OH-	8.94309E-05				
Temp.(C)	12				

MINERALS FORMED

MINERAL	SAT.INDEX	MOLES	MINERAL	SAT.INDEX	MOLES
calcite	8.39233E-05	1.50467E-04	quartz	6.86169E-02	not assessed
dolomite	.014534	8.10057E-04	goethite	4.0635	not assessed
boehmite	.387662	not assessed	albite	1.13943	not assessed
phlogopite	2.86464	not assessed	adularia	1.79918	not assessed
muscovite	4.32732	not assessed	talc	6.35411	not assessed
kaolinite	3.03434	not assessed	chlorite	18.5334	not assessed
illite	3.88318	not assessed	montmorillonite	2.49431	not assessed

TOTAL DETERMINAND CONCENTRATIONS

DETERMINAND	ORIGINAL	FINAL	DETERMINAND	ORIGINAL	FINAL
calcium	9.70057E-04	9.53338E-06	magnesium	8.20249E-04	1.01925E-05
sodium	1.08187E-02	1.08187E-02	potassium	9.03337E-05	9.03337E-05
chloride	8.6873E-04	8.6873E-04	alkalinity(asHCO3)	1.22791E-02	8.73791E-03
sulphate	1.19601E-03	1.19601E-03	aluminium	6.0131E-04	6.0131E-04
iron	1.51472E-06	1.51472E-06	nitrate	4.77285E-04	4.77285E-04
silica	1.74894E-04	1.74894E-04	boron	1.36209E-05	1.36209E-05
ammonia	1.50499E-05	1.50499E-05			
pH	10.5072	10.344			
ionic strength	1.70502E-02	.013758			
charge error (%)	1.18294	1.36646			

All concentrations expressed in moles

date : 14/10/85 time : 12:44:33
elapsed secs: 1261 cpu used: 1092.5

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